INFRARED DETERMINATION OF ORGANIC STRUCTURES

H.M. RANDALL · R.G. FOWLER · N. FUSON · J.R. DANGL

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PREFACE

Investigators, whether they are chemists, biochemists, or physicists, using infrared spectra to determine molecular structure have found little published data covering this type of work. The authors believe the material of this text will add very substantially to the available information in this rapidly expanding field. Since the methods of infrared analysis in determining the structure of chemical compounds at present are largely empirical, the certainty with which predictions of structure can be made depends greatly on the information and experience of the investigator. It is the plan to supply herewith some of the background which is required.

To this end, methods of approach have been outlined; the possibilities inherent in the method have been explored; currently established correlations between structure and the absorption spectrum have been itemized; the instruments and techniques have been described. In Chapter III, a unique tabulation is made of the assignments of absorption bands for a large number of compounds containing double bonds. In Chapter IV, the results of years of work on molecular structure are compiled in a form easily usable by nontheoretical chemists and physicists. Chapter V offers illustrations of the *modus operandi* for proceeding from the measured absorption spectrum to its interpretation in terms of molecular structure. Finally, the actual records of a great variety of compounds are reproduced for their reference value as a library. The over-all attitude of the authors has consciously been held nearer to that of the organic chemist than that of the molecular physicist.

During the war years of 1942–45, the authors formed one of the many governmentally sponsored research groups in this country and in England whose objective was to determine the structure of penicillin and, if possible, synthesize it. In order to become sufficiently oriented for effective work, it was necessary to study spectra of many compounds, not all directly related to the penicillin molecule in structure, but largely all of the common family of aliphatic or phenyl substituted aliphatic compounds. Because of this trend in the choice of compounds, no claim is made to a complete treatment of the present status of infrared spectroscopy, even in its application to molecular structure.

Nevertheless, the book should be of value to anyone interested in the way that infrared analysis is done and the extent to which it can be helpful in chemical problems, coming as it does at a time when the infrared method is rapidly penetrating the chemical and pharmaceutical industries, especially as applied to research and control in the chemistry of petroleum, rubber, plastics, medicinals, and dyestuffs. Wherever a spectrograph exists, such research problems as are surveyed here can be met and advanced.

The authors accordingly present this work with the belief that, although the material was obtained in furtherance of a limited objective, it will nevertheless help in the solutions of problems in very diverse fields.

The authors, being primarily physicists, had frequent recourse to the knowledge of others for chemical information. In this respect they wish to acknowledge gratefully their indebtedness to Professors Werner E. Bachmann and Peter A. Smith of the Department of Chemistry, University of Michigan, for many special compounds which they made available. Our gratitude is also due to Dr. Otto Wintersteiner and the E. R. Squibb Laboratories, to Dr. Jack Hinman and the Upjohn Laboratories, and to Dr. Karl Folkers and the Merck Laboratories for a number of the compounds in the catalogue.

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Chapter I

THE APPLICATION OF INFRARED SPECTROSCOPY TO CHEMICAL ANALYSIS

Introduction

The growing importance of infrared spectroscopy in industry is evidenced by the increasing number of industrial laboratories which employ this type of spectroscopy as a tool to further their research programs. One factor which has limited the rapidity of this increase has been the lack of adequate commercial spectrographs, amplifiers, recorders and supplementary equipment specially designed to meet the requirements of this kind of work. This difficulty seems to be in the process of being eliminated, for both spectrometers and spectrophotometers along with their attendant equipment are now becoming available.

Many infrared installations in industrial laboratories are concentrating on the quantitative analysis of mixtures of compounds which are difficult to resolve chemically, such as stereoisomers, cis- and trans-isomers, and especially compounds of similar boiling point. The utility of this method depends upon the uniqueness of the spectra of individual organic compounds. Since no two organic compounds possess completely identical spectra, the variant bands may be used to estimate concentration by employing Beer's law, which establishes the relation between intensity, concentration and thickness of the absorbing layer.

Even qualitative identification of the components of a system may be of interest and importance, and for this purpose the methods of infrared spectroscopy are often particularly useful. If a large enough library of spectra is available, it is possible to identify compounds and, in favorable instances even mixtures of compounds, by comparison with such reference spectra. For this purpose a card file or card-sorting device based on some number of prominent bands in the spectrum of each compound would be helpful, the value of the method increasing with the size of the library.

A third application which is receiving growing attention is the establishment of molecular structures. The basis of this development is empirical and rests on the observation that certain combinations of atoms, recurring frequently in complex molecules, may be associated with certain absorption bands in the infrared spectra of these substances. Examples of such groups are C=O, NH, and CH_3. Were the bands produced by each atomic group invariant and unique in their positions in the spectra of all substances containing the group, it would be immediately possible to determine the presence or absence of any group in a given molecule by the measurement of its infrared spectrum. Each compound, however, possesses its own spectrum. The other structures adjacent to a given group influence its electronic and spatial configurations. In addition, the masses of the other atoms involved in the vibration change from molecule to molecule. As a result, a given group may show somewhat different values for its absorption bands in the spectra of different molecules which contain it. Further, the bands due to one group in one compound may have the same wavelength value as an entirely different structural group in another compound. As a result, some degree of uncertainty may attach itself to the interpretation of bands suspected of arising from any particular group.

A complete test of a given molecular structure based on infrared data would result only if a

precise mathematical computation were able to predict from the structure the spectrum actually observed. Such a proof is possible only in the simpler molecules. It has been achieved for a number of such molecules where the intramolecular linkages were well known and only the orientation of these bonds and the interatomic distances were unknown. Here, assumptions concerning the unknown could be made and tested by computations of the frequencies and intensities of absorption to be expected. After a satisfactory agreement was attained between these measured and computed values, the structure was regarded as established.

The above conditions are never fulfilled for complex molecules. The absorption spectrum and limited chemical data are the only sources of information available. It is the intramolecular linkages that are sought, and there is little or no basis for computation. Even when the linkages are known, the complexity of the molecules which chemists and biologists find "interesting" defies such an approach. Under these conditions it is necessary to resort to empiricism and, by correlations between bands which occur regularly with recurring structural features throughout a series of compounds, to draw conclusions about structures.

Historical Background

New as the methods of infrared spectroscopy may seem to many, quite a considerable time has elapsed since the original discovery of the relation between chemical structure and absorption in this region of the electromagnetic spectrum. Before the turn of the century, Julius [1] * had shown that the methyl group is always accompanied by an absorption band at 3.45 μ. He observed also that the absorption spectrum of a molecule is not, in most cases, a simple sum of characteristic absorptions of its component parts. Aschkinass [2] and Ransohoff [3] found that a band at 3.0 μ seemed to be associated with the hydroxyl group, although the work of the latter on alcohols was open to question concerning the water content of his samples. Other investigators working at this period obtained spectra of quite a variety of compounds, but few offered valid identifications until Coblentz [4] published his remarkable researches in this field in 1905. Progress in infrared spectroscopy has at all times been governed by the progress in spectrometer design toward the necessary resolution and speed. The instrument which Coblentz applied to this work very nearly possessed the degree of resolution adequate for most chemical survey work.

With this spectrometer, Coblentz examined over a hundred compounds of great variety. He observed that nitrogen and oxygen when added to a hydrocarbon molecule usually cause intense absorption bands. He substantiated the identifications made by Julius, and added the observation that NH_2 was accompanied by absorptions at 3.0 μ and 6.0 μ, while N=C=S in thiocyanates seemed to be characterized by a band at 4.8 μ. He observed the striking bands at 5.8 μ in esters and acids, but drew no conclusions from them.

An important advance in the theory of molecular physics was made by the discovery of the fine structure of the water vapor spectrum by E. von Bahr [5] in 1913. The design of high resolution instruments at Michigan and the recording in detail of the fine structure of the spectra of many simple chemical molecules gave such impetus to theoretical studies that the chemical applications of the method were accorded limited attention.

Another factor which acted to hinder the application of infrared spectroscopy to chemical analysis was the lack of a rapid, continuous method of recording spectra. Beginnings in the construction of such recorders were made by Langley [6], Ångström [7], Ellis [8], and Moll [9] whose devices were, however, subject to undesirable amounts of zero drift and, in addition, quite slow in operation. In the modern spectrometer for chemical work, zero drift has been eliminated by interrupting the entrant beam of radiation periodically and amplifying the periodic pulses of energy produced by the receiver. The amplification has been accomplished in a number of ways by optical, combined electronic and optical, or purely electronic means. Speed has now been achieved by the improvement of amplifiers and receivers.

The demand for a suitable instrument, which has stimulated the current developments, is a consequence of the laborious survey efforts of many investigators using equipment of the earlier type. Weniger [10], in 1910, in a careful and extensive examination of alcohols, acids, esters,

* See end of chapter.

aldehydes and ketones, concluded that the strong band always present at 5.9 μ in the spectra of compounds having a carbonyl bond is associated with this bond. He found that the 3.0 μ band is certainly caused by the OH group in alcohols, but he erroneously supposed that the 6.9 μ band seen in so many compounds also comes from this group rather than from the methyl group which actually produces it. He noted the existence of a band at 9.6 μ in primary alcohols, 9.1 μ in secondary alcohols, and 8.6 μ in tertiary alcohols which could be used, because of these shifts, to determine the position of the OH radical in the molecule.

Schaefer and Schubert [11], in a series of papers, examined salts of complex anions, and found that these ions show very specific spectra involving several absorptions. Sulfates were found to have a principal absorption at 9 μ; nitrates at 7 μ; selenates at 11 μ; chromates at 11 μ; chlorates at 10 μ; bromates at 12 μ. Lecomte [12], in the true spirit of the structural spectroscopist, obtained spectra of scores of related compounds and studied them for common factors. Ellis [13] examined large numbers of compounds in the region from 0.5 to 3.0 μ in a search for harmonic series of which he discovered many.

One of the earliest applications of infrared spectra to the study of molecular structure of complex molecules was made by Ross [14], in 1926, when he examined the spectra of the pyrones in an attempt to decide whether the structure included a benzene type ring with tetravalent oxygen.

By 1928, the methods and course of infrared spectroscopy had become sufficiently determinate to warrant the publication of treatises on the subject. Accordingly, texts appeared by Lecomte [15], Rawlins and Taylor [16], Schaefer and Matossi [17], and Sutherland [18]. The theory of band spectra was dealt with in these books and also specifically in articles by Dennison [19] and recently in texts by Ta You Wu [20] and by Herzberg [21].

The industrial period in the application of infrared spectroscopy may be said to have begun in about the year 1936. Since this time its progress into commercial applications has been extremely rapid, owing to a nice congruence between the results which the method is capable of supplying and the questions which chemical industry has to offer it. Excellent discussions of this point have been given by Wright [22], Barnes [23], and others [24], [25], [26].

The Interpretation of Spectra

As previously stated, the locations of the absorption bands of a molecule are in general extremely sensitive to the molecular structure. Such a slight change as is introduced by stereoisomerism produces its alterations of the spectrum, especially in the crystalline state, while a more drastic difference, such as that between the cis and trans isomers of a compound, can remove, at times, almost all traces of similarity between spectra. Replacement of intermolecular crystal lattice forces by those between solvent and solute molecules produces shifts in the position of bands. Release of intermolecular forces as in vapor spectra likewise produces changes. In crystalline compounds, there may be extra absorption bands caused by the removal, through molecular interaction, of degeneracies which had existed in the free molecule.

All this presents a complex picture. However, some conclusions can be and have been made.[1] Certain groups of a molecule can be expected to maintain a degree of order under alteration of the compound, and many groups maintain a greater degree of order than might be expected. In a simple diatomic molecule, the frequency ν of vibration of the molecule—and consequently the position of its absorption band—depends upon the force constant k between the atoms, and the masses M and m of the two atoms, according to the relation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k(M+m)}{mM}}$$

In a more complicated molecule the natural frequencies of the molecule, which, when there is a change in electric moment, are also the absorption frequencies in the infrared, depend in a far more complex fashion on all the masses and all the force constants in the molecule. To have a band relatively stable in wave length associated with a given diatomic group in the molecule, such as a band at 5.75 μ with an aliphatic ester carbonyl group, it appears necessary that there be

[1] Barnes, Liddell, and Williams, "Infrared Spectroscopy, Industrial Applications," *Ind. Eng. Chem.* (*Anal. Ed.*) **15**, No. 11, p. 659.

something distinctive about the bond strength or masses involved in the group. These must be either large or small, compared with the C—C group. The inherent difficulty in the problem comes because the principal skeletal constituents of organic compounds, carbon, oxygen and nitrogen, are so nearly alike in mass and, to a lesser extent, in the strength of the bonds which they form. In general, then, the structural groups which can be expected to remain unchanged in their frequencies of vibration from molecule to molecule are: first, those involving hydrogen-stretching vibrations because of the small mass of the hydrogen atom; and, second, those containing double and triple bonds because of the increased bond strength. It may also be possible that bands due to groups including such massive elements as sulfur, phosphorus and the halogens can be tentatively identified as lying in rather narrow wavelength ranges.

Within the wavelength domain in which bands of each general class of vibrations (i.e., hydrogen-stretching, double-bond, etc.) may be found, bands of subclasses of vibrations (such as C=N, C=O, etc.) may range somewhat widely and even overlap. Because of this, only two types of knowledge are generally possible from infrared spectra. Each may help, however, to identify chemical structures. First, given a compound with a known double bond, it is usually quite easy to predict where the absorption band will lie. Thus, it is often a simple problem to distinguish, by means of the infrared spectrum, between a number of proposed structures for a compound, if one of these structures is certain to be correct. Second, given an absorption band, although it may be impossible to tell with certainty what actually caused it (since, for example, any band found between 5.5 μ and 6.5 μ may be due to a carbonyl group, but may also result from any one of a number of other types of bonds), it is possible to select a small number of alternative structural groups from which the band might arise. This information in combination with other evidence, both chemical and physical, may lead to comparatively rapid solutions of the problem of identification. For example, if the compound under investigation has a strong band at 6.0 μ, although one cannot say definitely that it results from a C=O or C=N group, one can say, however, that it is probable there is present either (1) a straight chain C=N, or (2) an acyl group affixed to a nitrogen atom, or (3) a conjugated acid group such as benzoic acid. Certain unusual ring structures containing double bonds, and probably other configurations at present unrecognized, may also have bands here. Nevertheless, the information, in conjunction with other information which can be gained from the infrared spectrum, in addition to the chemical knowledge often furnishes a guidepost sufficient for the identification of the structure of a compound.

Normal Positions

A classification of the known bands and their approximate positions has been prepared empirically. It has been found that, in general, the classifications normally made on a basis of the chemical nature of compounds also have considerable significance in the infrared spectrum. Thus, hydantoins behave similarly chemically, and they are also found to exhibit common peculiarities in the infrared. In general, no relation has been found between band location (i.e., bond strength) and chemical activity.

Carbonyl Groups. Carbonyl groups produce absorptions found anywhere from 5.45–6.5 μ. As a class of bands, they are by far the most stable in position (for a specific type such as esters), probably because they always result from chain-terminating groups. They are usually the strongest bands in this region (this 5–7 μ region is often called the "double bond" region) and are often the strongest in the spectrum. This fact in itself is helpful in identifying them. Any strong band between 5.5 μ and 5.9 μ is almost certainly due to a carbonyl bond. It has been found expedient to make the following divisions of these compounds.

Carboxyl groups

A. Acids, 5.7–5.9 μ
B. Esters, 5.70–5.80 μ
C. Carboxylate ions
    1. Metallic salts, 6.2–6.35 μ
    2. Amino acid zwitter ions, 6.2–6.4 μ

Carboxyl derivatives

A. Acid halides, 5.55 μ
B. Nitrogen derivatives
    1. Acid amides, 6.0–6.2 μ

2. N-monosubstituted amides (acyclic), 6.0–6.2 μ
3. N-disubstituted amides and N-acyl disubstituted amines, 6.0–6.1 μ

C. Thiolesters, 5.95 μ
D. Lactones, 5.5–5.7 μ
E. Lactams, 5.75–5.9 μ
F. Anhydrides (two bands), 5.4 μ and 5.65 μ

Other carbonyl groups

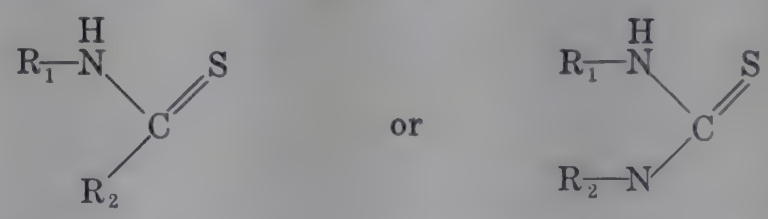
A. Ketones, 5.8–5.9 μ
B. Aldehydes, 5.7–5.8 μ
C. Urea type, —NH—CO—NH— (not definitely established)
D. Cyclic diacylimide type, —CO—NH—CO— (two bands), 5.6 and 5.9 μ

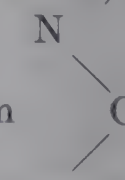
C=N Groups. Because of the trivalence of nitrogen these bonds are always found either in the interior of a straight chain or in a ring. In the one case in which the chain is terminated by hydrogen (C=NH), the influence of hydrogen bonding by the labile hydrogen is almost as pronounced as the presence of an extension to the chain would be. The vibrations of these bonds result in bands which are found usually on the long wavelength side of 5.95 μ. The only case in which the band, due to this bond vibration, has been known to be shifted to a shorter wavelength occurred when a charge was placed on the nitrogen atom.

Only a limited number of compounds having acyclic carbon-nitrogen double bonds have been examined. Among these were imino ethers, oximes, and guanidines. Bands for this vibration were found in general region 5.9–6.1 μ. No effort will be made to classify the vibrations here owing to the paucity of examples, and uncertainty of the exact structure of many of the prototypes, especially among the guanidines. A much larger number of cyclic compounds having carbon-nitrogen double bonds have been tested. In general, any ring compound with four or more ring elements shows no strong absorptions in the 5–7 μ region unless it has double bonds. Since the frequencies observed in a ring structure having conjugated double bonds are greatly altered from those of the corresponding acyclic double bond, it has been felt expedient to group absorption spectra of these ring compounds apart rather than to discuss them under the heading of the types of double bond which they contain. Unconjugated ring systems containing C=N bonds behave very much like open-chain systems, except that the absorption bands produced are usually much sharper in outline. Thus, the band resulting from the C=N group in thiazolines is found at 6.15–6.3 μ, a strong, sharp band. Substitution on the ring results in small influence on the wavelength of this band as long as no conjugation is introduced.

Carbon-Carbon Double Bonds. The situation with reference to the vibrations characteristic of these bonds is similar to that of the carbon-nitrogen type, with one exception. The carbon-carbon double-bond vibrations usually result in such a small change in dipole moment that the intensity of the infrared absorption is very low. Only when the C=C group terminates a chain, or is so situated that a nitrogen or an oxygen atom enters strongly into the same mode of vibration, is there a sufficient change of dipole moment to produce an intense band. The vibrations are always found on the long wavelength side of 6.0 μ. Ring compounds containing unconjugated C=C bonds were not studied in the course of this work.

Carbon-Sulfur, Nitrogen-Oxygen, Nitrogen-Nitrogen and Sulfur-Oxygen Double Bonds. The carbon-sulfur vibration itself cannot fall in the 5–7 μ region, because the mass of the sulfur is too great and the bond strength too small. Nevertheless, whenever the combination of a sulfur, carbon and nitrogen occurs either as



there is generally a strong band in the region from 6.2–6.8 μ. We have suggested that this arises from a carbon-nitrogen bond which would ordinarily be written as a single bond, but which is strengthened in the ionic form  probable for these compounds. This band will be termed a "thioureide ion" band.

Absorption bands due to nitrogen-oxygen double-bond vibrations have been identified at 6.4–

6.5 μ in various nitro-compounds, nitro methane, nitro toluene, nitro benzoic acid, and in the pentavalent nitrogen compound benzophenoxime methyl nitrone. Chloropicrin is an exception, with a band at 6.29 μ.

A few diazo compounds have been measured. The band corresponding to this configuration has not been identified from lack of model compounds, and because the diazo linkage had undergone structural rearrangement in at least one case.

Sulfates will not be included in the discussion of double-bond bands, since they do not occur in the same region with the others. A rather complex and intense absorption at about 8–8.5 μ characterizes the sulfates examined.

Single-Bond Invariant Groups. The hydrogen vibrations compose the major portion of this group and would produce the most stable bands in the spectrum were it not for the effect known as hydrogen bonding. This varies in an unpredictable fashion, and makes it impossible to distinguish between bonded NH and bonded OH vibrations. Little need be said about this class of vibrations, since so much is already known and written about them.[2] For the sake of completeness, however, the unassociated hydrogen-stretching vibrations, together with the spectral range of the absorption bands they produce, are given below:

OH	2.66–2.98 μ
NH	2.88–3.28 μ
SH	3.72–3.9 μ
OD	3.6 –3.8 μ
ND	3.85–4.15 μ
CH	3.05–3.7 μ

The associated OH and NH vibration bands range widely. Bands at 3.0–3.3 μ are found in alcohols, amines, and acids. In solid acids there is frequently a variety of bonding which is stable enough to produce a characteristic absorption. These absorptions are found from 3.6–4.0 μ and if present mask possible sulfhydryl vibration bands. In amino acids, amine hydrochlorides, and amino acid hydrochlorides a series of absorptions is found between 4.0 μ and 5.0 μ which appears to be characteristic of some bonded form of NH. For a further discussion of these vibrations the reader is referred to Chapter IV.

The only single-bond vibration between massive atoms which it is possible to use with any certainty is the C—O—C vibration, producing an absorption found in esters and ethers at 8–9 μ. It is recognizable chiefly from its intensity. Appearance of a strong absorption at this wavelength is far from a guaranty of the presence of such a configuration, but it serves well as a complement to the ester carbonyl bond absorption at 5.75 μ, in identifying this group.

The location of the C—S—C group bands might be expected to be similar to those of the C—O—C group in stability. Investigation has shown that these bands lie between 14 μ and 15 μ, and, hence, are indistinguishable by wavelength alone from absorptions produced by the bending vibrations of the carbon skeleton. Nor can they be distinguished by their intensity as in the case of the C—O—C group. Apparently, the increased mass of the sulfur reduces the extent to which it undergoes displacement in the vibrational motion, with a corresponding reduction in the change in dipole moment and absorption intensity.

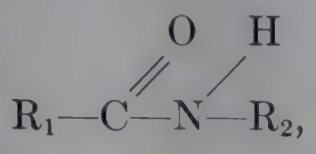
Absorption bands coming from NH bending vibrations are to be expected in the double-bond region. Primary amines actually do have a band of moderate absorption there (6.1–6.4 μ). Secondary amines do not show a band of any strength. Amino acids have bands, one of which may result from the NH_2 deformation vibration. It seems unlikely that strong bands observed in this region need ever be interpreted as caused by NH bending vibrations in the R′—NH—R″ structure and only occasionally as arising from NH_2 vibrations.

Special Invariant Groups of Unknown Mode of Vibration

In the compounds which have been examined, a few additional bands besides those already accounted for also fall in this region between 5.5 μ and 7.0 μ. Although there is reason in assuming that there is, in general, a one-to-one correspondence between strong bands in the region from 5–7 μ and the occurrence of double bonds in the molecule, nevertheless, exceptions are found. Some of the known exceptions which have been described are: (1) thioketo compounds, where the carbon-sulfur double bond which should have no

[2] Fox and Martin, *Proc. Roy. Soc.* **A175**, 208 (1941); *J. Chem. Soc.* 318–322 (1939); Norman Wright, *Ind. Eng. Chem. (Anal.*

band in this region exhibits one when in conjunction with nitrogen; and (2) primary amines. Other exceptions are found in the N-acylated amines and the amino acids. All acyclic compounds, having the structure



where R_1 and R_2 do not involve a carbonyl or imino group directly connected to the amide group, have two bands in the double-bond region. These are the carbonyl band at 6.0–6.2 μ and another band at 6.4–6.6 μ. No ordinary double bond exists in the configuration which will account for the second band. In like manner, amino acids show three bands in the double-bond region. The first band, at 6.0–6.1 μ, is probably from N^+H_3; the second, at 6.1–6.3 μ, is from CO_2^-; the third, at 6.60–6.70 μ, again has no obvious source in the structure. Further discussion of both of these classes of compounds will be made in a succeeding chapter.

Ring compounds should in the main be included in this category. Certain simple rings involving no conjugation behave in a manner analogous to the corresponding straight-chain compounds. Thus, the carbon-nitrogen double bond in thiazolines, pyrazolines, imidazolines, etc., can be recognized. Compounds having a high degree of conjugation like benzene, pyridine, thiophene, etc., exhibit double-bond bands, but no mode of vibration of the ring can be recognized, and substitution on the ring produces pronounced shifts in these vibrations. It is necessary to make subclassifications in regard to the location of substitutions on the ring. Lack of time and insufficiency of ring compounds have prevented this needed extension of the work.

The phenylacetyl group, $\varphi—CH_2C(=O)—$, has an interesting set of specific absorption bands at 13.3 μ and 14.4 μ with a third wandering band between these. The 14.4 μ band is extremely stable, and since absorptions in this region are not common, this group of absorptions can be used as an indication of the presence of a phenylacetyl radical. The 14.4 μ band is characteristic of the phenyl group alone.

All hydrochlorides have a number of sharp absorptions between 3.7–4.1 μ, sometimes welding into a complex band. This configuration is quite similar to that of an associated acid. It is generally quite difficult, with the low resolution of the salt prism, to distinguish between hydrochlorides and acids, and, as noted previously, these would always mask a sulfhydryl absorption. Higher resolution would enable one probably to map and interpret these absorptions. At one time it was felt significant that these bands occurred at about the same wavelength as that of the free HCl-stretching vibrations, but it is certainly only fortuitous.

That association bands may be located in the 5–7 μ region is illustrated by the spectrum of the compound morpholine. An extremely intense absorption was observed at 6.45 μ. Another band of equal intensity occurs outside the double-bond region at 7.4 μ. Solution spectra in chloroform, CCl_4, and hexane showed no trace of these bands, and revealed a complex skeletal spectrum from 7–15 μ which had been previously almost completely absent. N-methyl morpholine has no such absorptions, and morpholine shows no NH-stretching vibration bands at 3 μ. It was, therefore, concluded that these bands are association bands, probably resulting from the form NH—O, although the absence from the associated spectrum of bands caused by the skeletal and CH vibrations may indicate that the CH hydrogen atoms enter in also.

The above example illustrates two points: (1) Both solution and pure material spectra are desirable; and (2) it is unsafe to assume that a strong band between 5 μ and 6.75 μ is *always* caused by a double bond.

Tools for the Investigation

Although, at first thought, stability in wavelength seems an intrinsically desirable thing, actually it is an advantage in analysis that the bands are only stable to the first order of approximation, and, in the second order, still depend upon general molecular configurations. This permits one to make additional tests and obtain more information about the structure of a given molecule than merely the number and nature of the double bonds and hydrogen atoms in it.

Given, for example, a compound with a known

carboxylate group. By making a series of the acid, ester, and sodium salt of this compound, taking solid and solution spectra of all three derivatives (in both polar and non-polar solvents if possible), many conclusions can be reached from consideration of the location of the acid, ester, and ion carbonyl absorption, and from the shifts of these bands when the compound is run in solution. Double-bond bands in the molecule other than the carboxylate group bands also undergo telltale shifts in position when the nature of the carboxylate carbonyl is changed in this fashion.

The bands of all compounds undergo some shift in position when a solution spectrum is compared with a solid paste spectrum. It is therefore desirable to have a spectrum of the compound both in the solid state and in solution. A truly complete catalogue would include both types of spectra. It was impossible to take time under the pressure of the investigation in which the bulk of this information was obtained to run multiple spectra of each compound. Therefore, in general, each compound was used in its normal physical state.

Additional information about the bonds associated with the labile hydrogen atoms in a molecule (OH, NH, SH, etc.) can be obtained by replacing these atoms with deuterium. Several lines of approach have been tried on this problem of deuterizing compounds. Compounds containing the deuterium in the desired position have been synthesized. Compounds with ordinary hydrogen have been treated to displace the hydrogen with sodium, with subsequent displacement of the sodium with heavy water, or they have been treated directly with excess heavy water to induce displacement by mass action. Of these methods, the last has been as successful as any. Because the degree of deuterization has never seemed to be more than about 75 per cent, owing, it is presumed, to the universal presence of moisture in the air and on apparatus, another method was proposed but not tested for observing limited regions of the spectrum. This involves (1) direct treatment of the sample with either heavy water or heavy alcohol, removing solvent in vacuo, and (2) running a solution spectrum of the sample in either heavy alcohol or heavy water using cells with silver chloride windows.

Model compounds, of course, comprise the most effective aid to the identification of unknown structures as the degree of approximation to which the correct structure is known advances. But the model compounds are as much a hindrance as a help unless their structure is unequivocally established, for in better than three-fourths of the disagreements between the predicted infrared spectrum and the observed spectrum, the compounds have been found on subsequent chemical investigation to be failing either from decomposition, impurity, confusion, or incorrect structural assignment. In the rest of the cases, a new structure group is required. The authors have come, after many trials, to trust the infrared evidence on the minimum number of double bonds, the general nature of these bonds and the presence of NH or OH groups, more than the chemical reputation of the compounds.

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Chapter II

INTERPRETATION OF SPECIFIC STRUCTURE GROUPS AND METHODS FOR RECOGNITION OF THESE GROUPS

To illustrate the general methods described in the previous chapter, several types of structures having reliable behavior have been chosen, and the factors which influenced the interpretation of them will be discussed. Special attention has been given to those structures which exhibit more than one invariant band.

Interpretation of Amides

As the first structure, consider the amides. If the term "amide" is made to embrace all compounds of the type R—CO—N(R′)(R″), the term "amide group [3]" will be understood to be restricted to the —CO—NH— group in the acyclic compounds of the type R—CO—NH—R′, in which R′ involves no carbonyl adjacent to the amide group NH, and R involves no NH adjacent to the amide carbonyl.

Amides naturally divide themselves into three classes, both from the chemical standpoint and from their infrared properties. These are (1) true amides R′=R″=H, (2) monosubstituted amides (the amide group) R″=H, R′≠H, and (3) disubstituted amides R″≠H, R′≠H.

All amides have a very strong band at 6.0–6.2 μ (with a few unusual exceptions outside of these limits) which it is reasonable to associate with the carbonyl vibration because of its intensity and because it is ordinarily the shorter wavelength band characteristic of and common to all amides, which occurs in the double-bond region. This common feature of the spectrum unites the classes. It is the only feature of importance in the spectrum of the disubstituted amides.

Unsubstituted amides have two to four significant bands added to this basic band. There are usually two bands at 3 μ, caused by stretching of the NH_2 group. There is always a band of less intensity than the carbonyl group band in the double-bond region. This band occurs in the immediate vicinity of the carbonyl group band, is frequently poorly resolved from it and may be found on either side of it. This weaker band seems likely to be caused by the NH_2 bending vibration, which is about the same intensity in primary amines. No proof of the assignment is given, but a band is to be expected in this region from such a source. A fourth band, the significance of which is important to the theory of the spectra of monosubstituted amides even though it is outside the double-bond region, is usually to be seen between the CH_2 and CH_3 bending vibration bands at 6.8 μ and 7.3 μ. In the seven amides examined it lay between 7.05 μ and 7.15 μ with the exception of malonamide in which it was absent. It is believed that this arises from the C—N stretching vibration. This has been computed as falling near here by Rasmussen and Brattain.

Monosubstituted amides form a remarkable group of compounds on which a great amount of work was done owing to their importance in the OSRD penicillin program. The compounds of this type have two bands of known source other than the carbonyl group. There is a band at

[3] In the course of the OSRD penicillin program Messrs. Brattain and Rasmussen of the Shell Development Company, Emoryville, California, first pointed out that this group has two bands associated with it in the double-bond region.

3.0–3.15 μ for the NH-stretching vibration and a band at 6.4–6.6 μ which is believed to be caused by the C—N stretching vibration. The three bands are very reliable in their positions and, as a set, are an excellent criterion for determining the presence of this group.

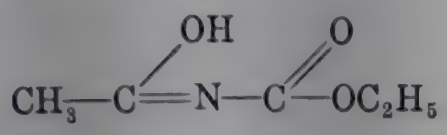
The band at 6.5 μ is one of the few discovered violations of the rule that there is a one-to-one correspondence between double bonds and absorption bands falling betweeen 5.4 μ and 6.8 μ. Accordingly, much effort was devoted to explaining the origin of the band in the molecule. It was first established that the band is always present in the spectrum when the group $R—(\overset{O}{\overset{\|}{C}}—\overset{H}{\overset{|}{N}}—)R'$ is present in the molecule, provided there are no cyclic connections by way of the R groups (as lactams) and provided the R groups have a carbon adjacent to the amide group. The second restriction can be liberalized somewhat because compounds have been examined in which R′ was the piperidine ring attached to the amide group by the ring nitrogen without compromising the effect. Furthermore, some N-substituted urethanes exhibit both bands of the amide group. These last results are valuable to the theory since they indicate that the origin of the three absorptions is certainly resident in the amide group itself and not in its external linkages.

Three explanations have been brought forward to account for the two bands of the amide group in the 6 μ region. (For brevity these two bands at 6.1 μ and 6.5 μ will often be referred to hereafter as the Amide I and Amide II bands respectively.) No one of them has been made to explain all the known phenomena. Briefly the hypotheses are: (1) that the two bands arise separately from two coexistent forms of the amide, i.e., enol and keto forms; (2) that the 6.1 μ band arises from the carbonyl group and the 6.5 μ band from the bending vibration of the NH group; (3) that the 6.1 μ band results from the carbonyl vibration and the 6.5 μ band from the natural stretching vibration of the C—N group enhanced in bond strength by circumstances of geometry and perhaps by sharing of the bond strength of the carbonyl.

In support of the first hypothesis, a number of arguments have been presented. In the first place, such an assumption would maintain a one-to-one relationship between double bonds and bands in the double-bond region as would be preferred. In the solid state, the two double-bond region bands appear to be independent of one another—i.e., in going from one compound to another, the relative changes in position and intensity vary without correlation. In the spectra of various compounds, these changes in relative intensity could be easily explained if varying proportions of the enol-keto forms were postulated. Furthermore, the absence of the longer wavelength band in the spectra of lactams could be explained as readily. Probably the most important support for this assumption comes from the fact that the deuterization of N-ethyl acetamide and N-methyl benzamide apparently gives two bands near 4.0 μ, which has not been readily explained by any other hypothesis than this. Here it could be assigned to OD and ND stretching.

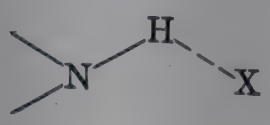
The fact that an intermixture of keto-enol forms is required under this hypothesis provides one of the strongest arguments against this explanation of the two bands. If this assumption were correct, it would require the existence of an admixture of anisomorphic forms of a compound in one crystal lattice. It should, moreover, be possible to alter the proportion of these two forms. Experiments carried on with N-methylbenzamide apparently show that the observed phenomenon is monomolecular rather than bimolecular. Using the usual technique, N-methylbenzamide was deposited upon a salt plate from acetic acid, water, chloroform, benzene, carbon tetrachloride, acetone, ethanol, methyl cellosolve, and pyridine, and the spectrum recorded. No change was observed, within experimental error, in either the position or intensity of the Amide I and Amide II bands, which appear in all cases, at 6.01 μ and 6.43 μ, respectively. If the two bands had arisen from enol-keto forms, intermixed in the crystal, the band intensities would be expected to change, as the various solvents used should have forced the compound to be crystallized in varying proportions of enol and keto configurations. Still another argument that has been advanced by Brattain and Rasmussen against this hypothesis is that the bands are not in the positions to be expected from a keto carbonyl or an enol C=N bond, but are at longer wavelengths. (The expected positions of

such bands are closer to those of unperturbed C=O and C=N vibrations at about 5.7–5.8 μ and 6.0–6.1 μ, respectively.) In support of this latter argument, the spectrum of acetyl urethane may be cited. The compound appears to be completely enolized into the configuration



and shows two strong bands in the double-bond region, one at 5.86 μ and the other at 6.20 μ, the usual positions for bands arising from conjugated ester carbonyl and conjugated C=N vibrations, respectively. This indicates that the 6.50 μ band is at much too long a wavelength to result from an unperturbed C=N bond, and the same conclusion would be valid for the band at 6.0–6.10 μ with respect to an unperturbed C=O bond.

The second hypothesis is that the Amide I band is caused by a C=O stretching vibration and the Amide II band by an NH bending vibration. Two major arguments have been presented in favor of this hypothesis. First, the longer wavelength Amide II band decreases in intensity upon deuterization, and, second, the changes in position of this band between solid and solution in the few cases which have been examined agree qualitatively with the changes to be expected upon releasing the N—H bond from an associated form



to an unassociated form.

Amide solution spectra recorded at the University of Michigan did not show any appreciable shift to shorter wavelength for the Amide I band. The shift, was, however, found by the Shell laboratories, working with more dilute solutions.

On the other hand, this hypothesis does not explain the absence of the Amide II band from the spectra of the lactams. Also it seems highly improbable that the band should be present in the spectra of the amides and absent, as in fact it is, in the spectra of the secondary amines, if an NH bending vibration is the source of the Amide II band.

The decrease of the Amide II band in intensity upon deuterization is in accord with this hypothesis. However, while examination of the spectra of deutero-N-methyl benzamide and deutero-N-ethyl acetamide does show a band in the vicinity [4] (8–9 μ) in which the ND bending vibration band would be expected, this band is far too weak to account for the loss of intensity in the Amide II band upon deuterization. The only new strong band appearing in the spectra of the deuterized compounds at longer wavelength than 6.4 μ occurs at approximately 6.8 μ in deutero-N-ethyl acetamide and at 6.83 μ in deutero-N-methyl benzamide. These bands are at a longer wavelength than the original band by approximately a ratio of 1.04, which is the order of magnitude shift to be expected for a vibration involving motion of the nitrogen and hydrogen as a unit when deuterium is substituted for the hydrogen. This result leads directly to the last hypothesis which seems likely to be the most valid of the three.

In the third hypothesis, it is assumed that the two bands arise naturally from normal vibrations of the group: R—CO—NH—R′. The x-ray study of acetamide by Senti and Harker [5] indicated a bond length of 1.38 A for the C—N bond, much shorter than the usual covalent bond length, which is usually about 1.47 A. This indicates a bond strength between that of a covalent single bond and a normal double bond, probably giving rise to the strong absorption at 7.1 μ, which appears in the spectra of NH_2 amides, but not in the spectra of their monosubstituted derivatives. Calculations by Rasmussen and Brattain on acetamide, using the bond strengths derived from the studies of Senti and Harker, predict normal vibrational frequencies very close to those observed in the spectrum, but of somewhat longer wavelength. For example, the calculated value of the vibrational band found at 7.15 μ is 7.40 μ. This would not necessarily indicate that the calculations were incorrect, but more probably that the bond strengths were incorrectly estimated, being even stronger than the original estimates. The vibrational frequencies of N-methyl formamide were calculated using the same bond constants as those given for acetamide by Senti and Harker. The resulting frequencies for the two modes of vibration which involve primarily the C=O and

[4] Work by Edsall and Scheinberg [*JCP* **8**, 520 (1940)] on the spectra of deutero-amines and hydrazines indicates that the ratio in wavelength between ND and NH bending vibrations is of the order of magnitude of the $\sqrt{2}$.

[5] *J.A.C.S.* **62**, 2008 (1940).

C—N bonds are still essentially the same as for acetamide. This indicates that if bond strength changes are neglected, monosubstitution onto the nitrogen in amides has little effect on the amide group frequencies.

As was mentioned before, the deuterization experiments closely coincide with the changes to be expected in the spectra with the greater mass of the deuterium atom substituted for the hydrogen on the nitrogen, the NH and ND group vibrating as a unit. This shift, observed in the spectra of deutero-N-ethyl acetamide and deutero-N-methyl benzamide, was of the same order of magnitude as that observed by Edsall and Scheinberg,[6] who found shifts in wavelength of the ratios 1.038 and 1.024 for bands associated with the C—N bond of deutero-methyl amine and deutero-methyl amine hydrochloride, respectively. The explanation of the new band appearing in the spectra of the deutero compounds appears difficult to render on any basis other than this.

It seems very possible that the weak band which appears at 8–9 μ in the spectra of the deuterized amides results from ND bending vibrations and that the NH bending vibration band which corresponds to it is a weak component of the 6.4–6.6 μ band at all times. In fact, Sutherland [7] has reported resolving this 6.5 μ band into two components in the case of N-ethyl acetamide.

Further work will certainly be desirable on this point, especially in the light of the fact that no single hypothesis has yet been made to account fully for all known phenomena in the spectra of the amides.

Recognition of Amides

The ability to recognize amides is a rather valuable contribution of the infrared method since there are no very easy or satisfactory chemical tests for this group. Success in recognizing this group depends on the number of stable bands associated with it, the rather unusual position of some of these bands, and the relatively small chance that another compound will have so many bands each of special origin.

Disubstituted amides have only one absorption band, arising from the carbonyl group. It is therefore quite difficult to do more than include this group as an alternative structural possibility when there is a band occurring at 6.0–6.1 μ with no other bands in the spectrum which could alter its significance. Some aid may be had from the fact that a band caused by this type of carbonyl group is always strong and quite broad.

If there are bands at 3.0–3.15 μ, 6.0–6.2 μ and 6.4–6.6 μ, a good first assumption is that an amide group is present. Further confirmation of this may be had by deuterizing the compound by exchange with heavy water or alcohol, when the 3 μ band will shift to 4 μ and the 6.5 μ band will shift to 6.8 μ.

For NH_2 amides, the duplex nature of the 3 μ band and of the band between 6.0 μ and 6.2 μ (with one member always of about one-half to one-third the intensity of the other) when found together with a fifth band at 7.05–7.15 μ should go a long way to establish their nature. Further tests can be made by deuterization, when all of these bands except the strong 6.0–6.2 μ band should undergo shifts of varying degree.

Recognition of Amido Acids

A compound containing both an amide and an acid group will be described as an amido acid. It is found that the absorptions corresponding to the two groups are usually in their normal positions. A number of peculiarities make it possible, however, to identify compounds of this type with some certainty and even, to a degree, to determine the relative positions of the two groups in the molecule.

Amido acids can be established by comparison of the spectra of acid, ester and salt. In most of the cases studied, the Amide I band of these derivatives was found to be shifted to shorter wavelength with respect to its position in the acid. In those compounds whose methyl esters were solids, the characteristic bands fall in groups having very narrow limits: 3.05–3.10 μ, 5.75–5.80 μ, 6.09–6.12 μ, 6.41–6.46 μ. Liquid methyl esters show a shift of the first three bands to shorter, and the last band to longer, wavelength. Solid ethyl esters seem to possess the same attributes as liquid methyl esters, since the same effects are found in both groups.

Alpha-amido acids may be recognized, after the general identification has been made, by means of the location of the Amide I band in the

[6] Edsall and Scheinberg, *op. cit.*, p. 524.
[7] Official report, Committee for Penicillin Synthesis.

acid spectrum. For all acids studied, this band was found to lie on the long wavelength side of 6.18 μ only in the spectra of alpha substituted acids. The bands of acids substituted on another carbon were all found to lie on the short wavelength side of this value. In like manner the acid bands of alpha acids all occur on the short wavelength side of 5.90 μ, with all others on the long wavelength side.

Two or more broad absorptions which may or may not be specific to the amido acids are observed between 4 μ and 5 μ. Their origin is unknown. Amido acids are the only compounds of established structure in which they have been observed so far. A somewhat similar set of different contour occurs in the amino acids, however.

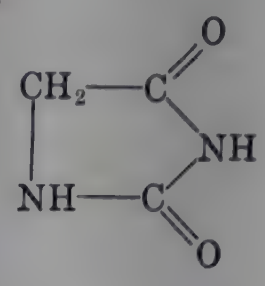
Interpretation of Ring Type Diacylimides

The class herein called cyclic diacylimides comprises compounds possessing the group

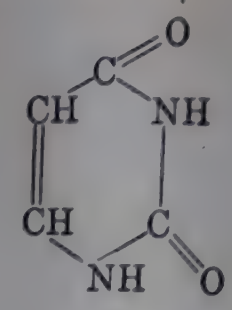
—CO—NH—CO—

without apparent restriction on the rest of the molecule. Included among the compounds of this type which show common properties in the infrared are succinimide, the hydantoins, thiohydantoins, uracils, thiouracils, dihydrouracils, purines, etc. The comparatively high melting points of all these compounds might lead one to suppose that the absorption spectrum of the compound in the crystalline state would not be that of the molecule itself but would be related in some general way to the crystal structure. Actually, in all the cases which have been examined, solution and solid spectra of these compounds have checked within very close limits. The correlation of bands to structure, while not as good as in the case of the amides, is still better than would be expected if there were strong interactions involving the molecular groups taking part in the characteristic absorptions.

In the simple diacylimides like the hydantoins and succinimide, two bands are found, one between 5.6 μ and 5.8 μ and the other between 5.85 μ and 6.00 μ. Since, when a sulfur atom is used to replace the oxygen in the 2 position, the absorption at about 5.7 μ remains in the same range of wavelengths, it has been associated with the carbonyl bond in the 4 position and has therefore been termed the 4 position carbonyl band. It is certainly a carbonyl group band from its position alone.



Hydantoin



Uracil

That there is no bonding between the NH groups and carbonyl groups is shown again by the insignificant effects on the spectrum when these hydrogen atoms are replaced by methyl groups, as in 3-methyl hydantoin, or when the NH at the one position is replaced by CH_2 as in succinimide.

In the interpretation of the band falling at about 5.9 μ, as far as position alone is concerned, it would be possible for the molecule to enolize with the 1 position NH to give a C=N in the ring. That this is probably not the case and that this band is a carbonyl group band as well is shown by the spectrum of N-(n-amyl)-succinimide which has both bands as described. This absorption has therefore been termed the 2 position carbonyl band.

Recognition of Ring Type Diacylimides

There is a large overlapping between the location of the ordinary 4 position carbonyl band and the band of the average ester carbonyl, even though in a good part of the diacylimides the band is at a shorter wavelength than is common among ester group bands. These groups are thus difficult to distinguish from each other on the basis of this band alone. The ester group band range is rather sharply terminated at 5.7 μ, and hence any bands from there down to 5.6 μ have some likelihood to be 4 position carbonyl bands. If a band occurs between 5.7 μ and 5.8 μ the relative rarity of compounds of this type would make the ester group the most logical possibility. Under these circumstances, the cyclic diacylimide should be borne in mind as an alternative structure group, but the matter can usually be easily decided on the other chemical and physical evidence such as melting point.

If an absorption band is present within each of the 2 and 4 position carbonyl group band ranges, and the one in the 4 position carbonyl band range falls at a wavelength shorter than 5.7 μ, there is

more certainty of the identification. The band in the 2 position carbonyl band range otherwise adds very little assurance, since so many groups can have bands in the vicinity of 5.9 μ.

Because the double-bond bands are not affected by the NH groups, deuterization will add no knowledge from the double bond alone. It may be that other bands, not in the double-bond region, will be found sensitive to deuterization in a useful fashion.

Since compounds of this type are comparatively rare, the principal function of the analyst here is to verify the nature of a suspected compound, and recognition degenerates into a statement that the spectrum is or is not in accord with what was expected.

Interpretation of Acid Spectra

No great effort was made to establish the extent to which the phenomenon of association governs the position of the acid carbonyl group absorption. In the few cases which were examined the shift from solution to solid was about .05 μ. While dimerization has been employed to advantage in explaining the spectra of the simpler acids (formic and acetic), it seems likely that as the molecule increases in complexity the monomeric form is the usual one.

Three varieties have been recognized among the carboxylic acids: (1) ordinary and thio carboxylic acids, (2) amino acid hydrochlorides, (3) amino acids. The last cannot properly be considered as acids since they always show bands caused by carboxylate ion groups, and hence should be discussed among the salts.

Ordinary acids and thio acids are alike in having two bands corresponding to the acid group, if there are no basic centers elsewhere in the molecule. One of these bands they have in common. This falls between 5.77 μ and 5.93 μ and comes from the carbonyl vibration. The hydroxyl acids have a second strong, poorly defined, almost general absorption in the 3.0 μ region, while the sulfhydryl acids have this corresponding absorption in the normal SH region at 4.0 μ. These absorptions are complex and are a result of stretching vibrations for OH and SH respectively in the associated state. Solid hydroxyl acids occasionally have an absorption at around 3.9 μ.

Amino acid hydrochlorides have a complex spectrum involving five distinct bands in the most general case. (Amino acid hydrochlorides will be understood to mean the hydrochlorides of any compounds which simultaneously contain NH or NH_2 and a carboxyl group. No other limiting or discriminating factors have been found so far. Even such compounds as thiazolidine 4-carboxylic acid, and the amino benzoic acids appear to be included.) A beginning has been made at interpreting the spectrum, but a number of apparent exceptions exist. First, a most peculiar feature is the acid carbonyl group band which is released from the carboxylate ion state as found in the amino acids, and takes the extreme position of 5.7–5.8 μ, completely overlapping that of the ester group. Second, there is an almost continuous series of moderately strong bands extending from 3.3–4.0 μ. This is the region in which hydrochlorides always have absorptions, but part of the absorptions are probably caused by the NH_3^+ group. Third, there is usually a band at about 5 μ of which no interpretation has been made, but which is absent in the spectra of NH_2^+ hydrochlorides such as sarcosine hydrochloride. Fourth, there is an absorption caused by what may be an NH_3^+ bending at about 6.25 μ in nearly all of these compounds. Fifth, there is a strong absorption at about 6.7 μ (called the Amino Acid HCl II band) in all those examined except sarcosine, proline and N-phenyl glycine hydrochloride, the NH_2^+ type of compounds.

Deuterization experiments would be very desirable to assist in unraveling these bands, but as yet none has been attempted. Bands in the vicinity 6.4–6.8 μ are always very interesting since this is not a very densely populated region. All the cases which were noticed seemed likely to be some form of single-bond carbon nitrogen-stretching vibration of increased bond strength. It will be instructive to see how far this holds true as more certain interpretations are made.

Recognition of Acids

Recognition of the free carboxylic acid is not an especially important function of the infrared spectroscopist since he competes at a disadvantage with a piece of litmus paper. Usually it will already be known to be present, and it is only necessary to fix on the correct band for this group

and limit the discussion to the balance of the spectrum. It is conceivable that the presence of a hydrochloride group might mask the presence of a carboxyl in the same molecule from some of the more elementary tests, but on the whole the standard methods of identifying ionic groups like these leaves little to be desired.

Acid group bands may be confused in the infrared with those arising from ketones, aldehydes, lactams, ring amides like the diacylimides, thiolesters, and a great variety of miscellaneous molecular groups. It is therefore of great advantage to eliminate them by the chemical tests. The greatest difficulty in interpreting several bands, all in this region, would arise from the possibility of having a polybasic acid in which the chemical investigation had as yet only discovered one acid group.

In summary, with a compound which has a band between 5.8 μ and 5.9 μ and a complementary band at 3.0 μ, one interpretation of the many possible is that an acid is present, and the interpretation can be speedily checked by reference to chemical evidence.

Since the amino acid hydrochloride carbonyl group bands overlap those of the ester group they could be considered as alternative structural possibilities were it not for the other bands which are generally found at the same time. Thus, it is necessary to have a complex absorption from 3-4 μ and a moderately strong absorption at about 6.2 μ in every case, and, in addition, bands at 5 μ and 6.7 μ if an NH_2 amine is present. Taking in consideration the chemical tests for acidity of the compound will nearly always dispose of the difficulty.

The Interpretation of Amino Acid Spectra

The amino acid spectra are characterized by a series of low-intensity bands lying in the region from 3.45 μ to approximately 4.0 μ, and by a band that has nearly 20% absorption and which lies in the region 4.25 μ to 5.00 μ. Neither N-phenylglycine nor sarcosine shows any trace of the bands in the 3.45 μ–4.00 μ region shown by the other amino acids. N-phenylglycine shows a broad, shallow absorption extending from 4.26–4.62 μ, and a broad band with maximum at 4.99 μ. Sarcosine shows a band at 4.08 μ and no trace of the longer wavelength band.

All NH_2 amino acids have some regularity in their absorptions in the double-bond region. There are three of these absorptions, the strongest being that correlated with the vibration of the carboxylate ion. This band appears within the limits 6.21 μ (α-amino-α-methylbutyric acid) and 6.38 μ (β-alanine and α-amino-n-caproic acid). The second of these bands (for brevity referred to as Amino Acid I) is definitely weaker than the ion group band and occurs at shorter wavelength, between the limits 6.11 μ (α-aminoisobutyric acid) and 6.21 μ (d-isoleucin). It appears only as part of the structure of the 6.21 μ band of α-amino-α-methylbutyric acid. In the spectra of α-amino-n-valeric acid and α-amino-n-caproic acid, this shorter wavelength band appears as part of a general absorption extending from 6.03 μ to the ion group band at 6.32 μ. There is an extra 6.06 μ band in the spectra of β-alanine and ϵ-amino-n-caproic acid. The third band (which will be called Amino Acid II) appears in the spectra of all the NH_2 amino acids examined, at a wavelength longer than that of the ion group band, its position being within the limits 6.47 μ (α-aminoisobutyric acid) and 6.66 μ (β-alanine and dl-β-phenylalanine). The intensity of this long wavelength band varies greatly from compound to compound.

Recognition of Phenyl Rings, and Conjugated Ring Structures in General

If the phenyl group represents more than a tenth of the size of a molecule (in massive elements) it will usually be comparatively easy to establish its presence from the three absorptions which it produces. These are the CH stretching vibration band, at 3.25–3.30 μ, and ring vibration bands at 6.18–6.23 μ and 6.67–6.72 μ. These are sharp bands, strong in proportion as the molarity of the phenyl group increases, and very stable in position. They are often lost on the sides of stronger bands and must be looked for carefully.

Whenever the phenyl ring is conjugated in any fashion a new ring vibration of about the same intensity is made active, and its absorption will be found at 6.30–6.33 μ in spectra such as benzamide, benzoic acid, diphenyl, benzal derivatives, etc. The presence of all four of these bands may be taken as a sure indication of the presence of a phenyl ring conjugated to some other double bond in the molecule.

While no similar uses were made of the bands of other ring structures, it seems certain that examination of large enough groups of derivatives of naphthalene, pyridine or thiophene, for example, would yield similar characteristic bands for the recognition of these structures. Napthalyl derivatives are of sufficient use in dye chemistry to justify such work, but most of the other structures will never find more than specialized application and the investigation can be made at the time.

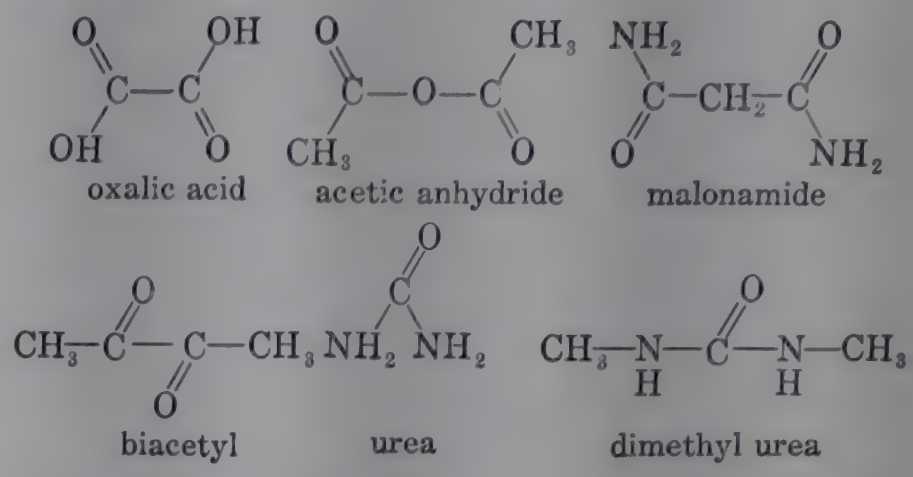
Groups Which Must Be Recognized from a Single Absorption

There is very little to add to the statements of Chapter I in regard to this subject. All that can be done is to make a tabulation of possible structure groups and eliminate the unlikely ones on a basis of additional chemical or physical evidence. The compounds which fall in this set at present are esters, salts, acid halides, thiolesters, disubstituted amides, lactones, ketones, and unconjugated C=N and C=C compounds.

One reason that these compounds are considered to have only a single characteristic absorption is that not enough work has been done on them to recognize other absorptions. This is certainly the case with the C=N and C=C groups. Each worker must extend the portion of the field in which he is most interested.[8] Esters always have a strong C—O—C group absorption at about 9 μ, but there is no secure way to recognize it as yet in complex absorption patterns. Acid chlorides must have a strong, long wavelength C—Cl absorption. In neither of the last two examples has any effort been made to establish a range in which the absorption caused by the vibration is to be found. If this were done, a band in this region could be called upon as necessary evidence to substantiate assumptions made from the lone double-band absorptions.

Symmetrical Molecules and the Repetition of Structure Groups in One Molecule

The empirical rules which have been developed thus far seem to be incapable of explaining the behavior of symmetrical molecules such as oxalic acid, acetic anhydride, malonamide, diacetyl urea, symmetrical diethyl urea, succinic acid, and many others.



A rule which succeeds in some cases, at least, seems to be that one band will be found at or near the established site for the band caused by a bond of the particular kind present singly in a non-symmetrical molecule, and a second will be found at longer wavelength.

The question of how far apart the similar groups must be before the symmetry is destroyed arises. In the case of dibasic acids of the series oxalic, malonic, succinic, glutaric, the symmetry is almost completely gone apparently when glutaric is reached and the two acid group absorptions coincide.

It will be nearly impossible to recognize a compound like malonamide by any of the rules discussed for amides. Hence, it seems likely that simple symmetrical molecules must be thrown into a special class and recognized by direct comparison between unknown and standard spectra.

To recapitulate: If a given group is repeated in a molecule and no interactions and symmetries are involved, the characteristic absorptions may be indistinguishable from those of a single group. If the two groups occur symmetrically placed, it will be necessary to recognize the cases individually without much assistance from the methods of structural analysis.

Conjugation Effects

When more than two double-bond groups are present in a compound, a number of curious effects may take place, none of which is clearly understood. If double bonds are widely separated in the molecule, they do not interact in most cases. Occasionally, an accidental superposition occurs which would not have been anticipated normally, and two bands are not resolved

[8] A useful group of papers illustrating the study of long wavelength absorption bands associated with the C=C group has appeared in the *Transactions of the Faraday Society*, **41**, 197–295 (1945).

where two are known to exist. Whether or not interaction has promoted this effect is uncertain.

When two double bonds are separated by a single bond, the bonds are said to be conjugated, and a known group of chemical phenomena is associated with this situation, particularly electronic absorptions in the ultraviolet. It has long been known to infrared spectroscopists that the presence of conjugation is accompanied by a shift from normal position for the bands of both bonds involved. This shift is from .1–.5 μ and is always toward longer wavelengths. It is believed that the bond strength of the intermediate single bond is increased at the expense of the two double bonds, but no proof of this is available.

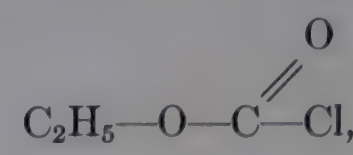
This shift effect applies to all the cases of conjugation examined except that between two carbonyl groups. Thus biacetyl, methyl pyruvate, and diethyl oxalate show no sign of conjugation, but only a single band at about 5.75 μ.

A third case is found in compounds like the ketenes, in which two double bonds are adjacent. Here a new band is introduced at very short wavelengths, whose indicated bond strength corresponds to that of a triple bond, about 4.75 μ.

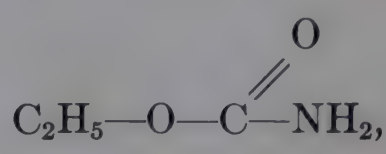
Conjugation must always be considered as a possibility whenever more than one band is observed in the double-bond region. Since it always produces shifts to longer wavelength, bands shorter than 5.8 μ usually can be left out of consideration. The intensity and shape of the bands involved must be used as a criterion if no other evidence is available. The ultraviolet absorption spectrum is, of course, a very valuable tool in this case.

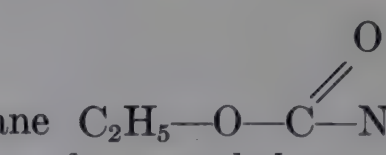
Groups of Multiple Significance

It is possible for a double bond to be placed in a molecule in such a fashion that it could partake of two structural interpretations. For example, in the compound ethyl chlorocarbonate



the carbonyl group may be regarded both as an ester and as an acid chloride carbonyl. Or in the compounds of the urethane series: urethane





methyl urethane $C_2H_5—O—C(=O)—NH—CH_3$, etc., the carbonyl can be regarded as an ester and an amide at the same time. Satisfyingly enough, the result in the infrared is that the carbonyl group band falls somewhere between the band positions which would be anticipated for either of the two groups. Thus the ester-acid chloride group band is at 5.60 μ, an ester group band being expected at about 5.75 μ and an acid chloride group band at about 5.5 μ. Likewise in the urethanes, the carbonyl group band falls at about 5.85 μ, midway between 5.75 μ (ester group band) and 6.0–6.2 μ (amide I band).

This desirable result plays havoc with the niceness of interpretations, however, and must be added to the effects of conjugation and symmetry as a source of difficulty in recognition of structure groups. The rarity of the phenomenon can largely be called into play to offset the handicap it imposes. Nevertheless, it must be borne in mind, and serves as another opening for imagination in the infrared.

Chapter III

A CATALOGUE OF EMPIRICAL STRUCTURAL ASSIGNMENT FOR THE DOUBLE-BOND REGION

Introduction

The purpose of this chapter and the succeeding one is to organize in a fashion which has proved helpful in structural investigations certain empirical and theoretical assignments which have been made. This chapter will comprise a tabulation of the empirical assignments in the double-bond region arranged according to wavelength. Using this kind of tabulation, the investigator may form some conclusions about the nature of unusual as well as usual structures which will give absorptions at a particular point, and the wavelength range in which a given absorption will be found. Preceding the complete wavelength tabulation (Table 2) is a short summary table (Table 1) which gives a résumé of the ranges over which special groups have been observed to absorb in the double-bond region. The chart given opposite page 20 is more graphic than Table 1 in summarizing spectroscopic information in the region from 2.7–7.0 μ.)

Assignment Terminology and Symbolism

Before describing in detail the symbols to be used in these tables, some explanation will be made of the terms used in referring to assignments. One of the striking manifestations of the cleavage between the methods of structural analysis as employed here and the more rigorous interpretations made by the methods of band spectra theory is in the terminology. This arises from the desire of the analyst to localize vibrations which the theoretical spectroscopist prefers to regard as associated with general modes of molecular vibration. The theoretical spectroscopist is concerned with the direction of the change of electric moment relative to the direction of the principal axis of rotation in the molecule. In this sense, all vibrations are regarded as including motions of every atom in the molecule. The structural analyst, being interested in identifying local structures in the molecule, tries to assign vibrations directly to such structures on the assumption that a particular structure contributes principally to each vibration. From this viewpoint, all vibrations are regarded as motions along or across the bonds joining the atoms and are spoken of as "stretching" and "bending" vibrations, respectively. As has been indicated before, this attitude is of fairly limited accuracy.

Most of the interpretative symbols used in Tables 1 and 2 are obvious from the discussion in the preceding chapters. However, some of the assignment symbols need brief comment. Symbols preceded by a "δ" refer to bending vibrations; all other symbols refer to stretching vibrations. δHOH and δNH_3^+ represent hydrogen vibrations of the hydrate group and the charged ammonia group respectively. "N-acyl C=O" refers to an amide carbonyl vibration, usually a disubstituted amide. "Anilino" refers to a vibration similar in origin to that of this frequency found in substituted anilines—possibly an enhanced phenyl ring vibration. "4 C=O" and "2 C=O" refer to vibrations of the 4 position and 2 position (urea) carbonyl groups respectively in cyclic diacylimides. "Carboxylate ion" refers to stretching vibrations in the group RCO_2^- whereas "thioureide ion" is believed to be an enhanced single bond C^+—N vibration in the thioureides (cf. Chapter I).

In addition to the rather specific interpretations above, in a number of instances it has been found that a group of bands in the 6 μ region will be characteristic of certain types of compounds, although the particular mode of vibration respon-

sible for the bands has not as yet been determined. In such cases these bands are listed and indicated as, for example, "benzothiazole I" and "benzothiazole II"; "amino acid I" and "amino acid II," etc. When particular modes of vibration can be securely assigned to some of the double-bond bands in a particular spectrum, but the sources of other of the bands in this region are not understood, the latter absorptions will be listed with the interpretation "unassigned."

Excluded from the catalogue of wavelengths (Table 2) are bands of the phenyl group. These bands will always occur at approximately 6.20–6.25 μ and 6.65–6.70 μ when such a group is present. An additional band always occurs at 6.30–6.35 μ when there is a conjugated phenyl group in the molecule. The catalogue has been ended, except for a few special instances, at 6.85 μ, the location of the intense band arising from the CH bending vibrations of paraffin oil.

TABLE 1. WAVELENGTH RANGES FOR INFRARED ABSORPTION BANDS ASSIGNED TO DIFFERENT VIBRATIONAL CONFIGURATIONS

Assignment	*Wavelength Range, microns*
*† Anhydride C=O	5.36–5.75
Lactone C=O	5.48–5.50
Acid halide C=O	5.52–5.54
*† Anhydride C=O	5.61–5.93
† Diacylimide 4 C=O	5.62–5.82
Ester C=O	5.68–5.81
‡ Amino acid hydrohalide C=O	5.69–5.80
Acid C=O	5.70–5.92
Aldehyde C=O	5.78–5.88
Conjugated ester C=O	5.78–5.92
Keto C=O	5.81–5.99
Joint ester and amide group C=O	5.81–5.99
N-acyl C=O	5.82–6.13
† Diacylimide 2 C=O	5.84–6.04
Conjugated acid C=O	5.89–6.02
Chain C=N	5.89–6.00
† Amide I (amide group C=O)	5.99–6.25
Chain C=C	6.02–6.11
δNH_2	6.08–6.25
‡ Amino acid I (δNH_2^+)	6.11–6.44
† Thiazole I	6.12–6.37
δHOH	6.12–6.19
‡ Amino acid I (δNH_3^+)	6.13–6.37
Carboxylate ion	6.16–6.38
† Phenyl I	6.20–6.26
‡ Amino acid hydrohalide I	6.21–6.29
NO_2	6.23–6.56
‡ Conjugated phenyl	6.30–6.35
‡ Benzthiazole I	6.31–6.62
Thioureide ion	6.31–6.92
† Amide II	6.39–6.67
‡ Amino acid II	6.47–6.67
† Thiazole II	6.50–6.70
Anilino	6.57–6.63
† Phenyl II	6.65–6.70
Deuterized amide II	6.80–6.90

* While the anhydride bands range widely, they nevertheless remain about 0.2 microns apart.
† One of two characteristic bands in this region.
‡ One of three characteristic bands in this region.

Explanation of the Assignment Catalogue (Table 2)

The first column gives the wavelength of each absorption in microns. The next column contains the corresponding frequencies in reciprocal centimeters or wave numbers. Column 3 records the intensity of each absorption band. Since only the strong bands are listed in this catalogue, the designations "w," "m," and "s" cannot be equated too literally to the usual understanding of the words "weak," "medium," and "strong." Actually, "s" bands are of the same order of intensity as the strongest band in the entire spectrum; "m" bands are about one-third to two-thirds as intense as the strongest band; and "w" bands are about one-quarter to one-third as intense.

Column 4 records the interpretation of the particular structural group involved and the localized vibration giving rise to the absorption band. The fifth column gives the name of the compound producing the absorption and the sixth column indicates by "S" or "L" whether the compound was in a solid or liquid state when the spectrum was measured. The last column tabulates the reference number for the spectrum of this compound to be found among the half-tone reproductions at the end of the book.

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
4.81	2079	s	C≡N	ammonium thiocyanate	S	187
4.86	2058	s	C≡N	guanidine thiocyanate	S	186
5.36	1865	w	anhydride C=O	succinic anhydride	S	163
5.48	1824	s	lactone C=O	2-phenyl-4-(p-methoxybenzyl)-oxazolone-5	S	162
		s	lactone C=O	2-phenyl-4-isopropyl-oxazolone-5	S	162
		s	lactone C=O	2-benzyl-4,4-diethyl oxazolone-5	S	161
		s	anhydride C=O	acetic anhydride	L	163
5.49	1821	s	C=O	2-phenyl-4-isopropylideneoxazolone-5	S	161
5.50	1818	s	lactone C=O	2-phenyl-4-isobutyl-oxazolone-5	S	162
		s	lactone C=O	2-phenyl-4-benzyl-oxazolone-5	S	161
5.52	1812	s	acid halide C=O	acetyl chloride	L	124
		s	acid halide C=O	acetyl bromide	L	124
5.54	1805	s	acid halide C=O	phenacetyl chloride	L	125
5.60	1785	s	joint ester-acid halide C=O	ethyl chlorocarbonate	L	107
5.61	1782	s	anhydride C=O	succinic anhydride	S	163
		s	acid halide C=O (conjugated)	benzoyl chloride	L	124
5.62	1779	w	4 C=O	allantoin	S	174
5.63	1776	m	4 C=O	hydantoin	S	173
5.65	1770	w	4 C=O	succinimide	S	171
5.66	1767	s	4 C=O	5,6-dihydrouracil	S	179
		w	4 C=O	N-(n-amyl)-succinimide	L	172
5.68	1761	m	4 C=O	1-methylhydantoin	S	174
		w	unassigned	uracil	S	179
		s	ester C=O	ethyl trichloroacetate	L	107
		s	C=O lactam	α-methyl-β-phenyl-β-anilino propionic lactam	Sol. in $CHCl_3$	163
5.69	1757	s	diester C=O	di-ethyloxalate	S	110
		s	acid C=O	sarcosine hydrochloride	S	228
		s	4 C=O	1-phenacetyl-2-thio-5,5-dimethyl-hydantoin	S	174
		s	4 C=O	1-phenacetyl-5 (N-benzylacetamido-methyl)-2-thiohydantoin	S	175
		s	ester C=O	2-benzyl-4-carbethoxyimidazoline-1-acetic acid ethyl ester	Sol. in $CHCl_3$	218
5.70	1754	m	ester C=O	monoethylphenacetamidomalonate	S	130
		s	4 C=O	1-acetyl-2-thiohydantoin	S	177
		s	ester C=O	ethyl hippurate	S	135
5.71	1754	s	ester C=O	N-phenacetylsarcosine methyl ester	L	156
		m	acid C=O	N-phenacetyl-N-phenylglycine	S	155
		s	4 C=O	barbituric acid	S	181
		s	ester C=O	N-phenacetyl-N-phenylglycine methyl ester	L	155
		s	ester C=O	α-phenacetamido-β-β-dimethoxypropionic acid methyl ester	L	128

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	ν	I	Assignment	Name of Compound	State	Spectrum Page No.
5.71	1754	s	acid C=O	*dl*-α-amino-α-methylbutyric acid hydrochloride	S	226
		s	ester C=O	methyl carbonate	L	107
		s	ester C=O	N-acetylthiazolidine-4-carboxylic acid methyl ester	Sol. in $CHCl_3$	109
		s	ester C=O	2-benzyl-4-carbethoxyimidazole-1-acetic acid ethyl ester	S	218
5.72	1748	s	ester C=O	methyl α-phenacetamido-n-caproate	L	139
		s	acid C=O	*dl*-alanine hydrochloride	S	226
		s	acid C=O	hippuric acid	S	135
		s	4 C=O	5-methyl-2-thiohydantoin	S	177
		s	ester C=O	butyl acetate	L	113
		m	4 C=O	3-methylhydantoin	S	175
		s	ester C=O	ethyl phenaceturate	S	137
		s	anhydride C=O	acetic anhydride	L	163
		s	acid C=O	2,2-dimethylthiazolidine-4-carboxylic acid hydrochloride	S	212
		s	keto C=O ester C=O	methyl pyruvate	L	166
		s	C=O	phenacetylurethane	S	159
5.73	1745	s	ester C=O	diethyl thiophenacetamido malonate	S	111
		s	acid C=O	pyruvic acid	L	104
		s	ester C=O	methyl phenaceturate	S	136
		s	ester C=O	methyl-2-benzylthiazoline-Δ^2-4-carboxylate	L	108
		s	acid C=O	α-aminoisobutyric acid hydrochloride	S	226
		s	acid C=O	*dl*-α-amino-n-valeric acid hydrochloride	S	227
		s	ester C=O	N-acetylthiazolidine-4-carboxylic acid methyl ester	L	109
5.74	1742	s	4 C=O	1-benzoyl-2-thiohydantoin	S	177
		s	4 C=O	1-benzyl-5,6-dihydro-2-thiouracil	S	178
		s	ester C=O	*l*-N-phenacetylproline methyl ester	L	157
		s	ester C=O	acetylcholine bromide	S	188
		s	acid C=O	phenacetamidomalonic acid	S	130
		s	β-lactam C=O	α-methyl-β-phenyl-β-anilino propionic lactam	S	163
5.75	1739	s	ester C=O	ethyl α-allylphenaceturate	S	110
		s	ester C=O	*dl*-N-phenacetylvaline methyl ester	L	145
		m	ester C=O	methyl α-phenacetamidoisobutyrate	S	140
		s	ester C=O	methyl ϵ-benzamidocaproate	L	137
		s	acid C=O	cysteine hydrochloride	S	227
		s	ester C=O	ethyl acetate	L	113
		s	keto C=O (cyclic)	cyclopentanone	L	167
		s	ester C=O (unconjugated moiety)	Δ^2 pyrazoline-3,4-dicarboxylic acid dimethyl ester	S	225
5.76	1736	s	ester C=O	N-phenacetyl-β-alanine methyl ester	L	133

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
5.76	1736	s	ester C=O	methyl α-phenacetamido-α-methyl butyrate	S	141
		s	ester C=O	ethyl hydantoate	S	110
		s	joint ester amide C=O	N-benzoyl-n-methylurethane	L	158
		s	ester C=O	ethyl formate	L	112
5.77	1733	s	ester C=O	thiazolidine-4-carboxylic acid methyl ester hydrochloride	S	108
		s	ester C=O	*dl*-N-phenacetylalanine methyl ester	S	142
		s	ester C=O	phenacyl acetate	S	107
		s	diester C=O	diethyl succinate	L	111
		m	4 C=O	2,4-dioxythiazolidine	S	211
		s	unassigned	benzoyl chloride	L	124
		s	acid C=O	*l*-tyrosine hydrochloride	S	229
		s	acid C=O	*dl*-α-amino-n-caproic acid hydrochloride	S	227
5.78	1730	s	ester C=O	N-phenylglycine ethyl ester	S	108
		s	ester C=O	methyl α-phenacetamido-n-valerate	S	134
		s	ester C=O	methyl δ-phenacetamido-n-valerate	S	132
		s	ester C=O	*dl*-N-phenacetyl-β-phenylalanine methyl ester	S	144
		s	ester C=O (conjugated)	ethoxymethylenemalonic acid	L	108
		s	acid C=O	*dl*-β-phenylalanine hydrochloride	S	228
		s	acid C=O	*l*-proline hydrochloride	S	228
		s	acid C=O	N-phenylglycine hydrochloride	S	228
		s	acid C=O	cystine hydrochloride	S	227
		s	4 C=O	alloxan (monohydrate)	S	172
		s	4 C=O	5-methylhydantoin	S	173
		s	aldehyde C=O	propionaldehyde	L	168
		s	4 C=O	5-(*o*-hydroxybenzal)-2-thiohydantoin	S	177
		s	4 C=O	5-benzal-2-thiohydantoin	S	176
5.79	1727	s	4 C=O	1-benzyl-5-phenacetamido-5,6-dihydro-2-thiouracil	S	179
		s	ester C=O	*d*-N-phenacetylisoleucine methyl ester	S	143
		s	ester C=O	2,4,6-trimethylphenaceturic acid methyl ester	S	145
		s	ester C=O	*deutero*-N-phenylglycine ethyl ester	S	108
		s	joint ester-amide C=O	N-methoxyurethane	L	158
		s	ester C=O (conjugated)	methyl benzoate	L	112
		s	acid C=O	N-phenylglycine	Sol.	122
		s	acid C=O	chloracetic acid	S	104
		s	carboxylic ester C=O	2-benzyl-4-carbethoxyimidazoline-1-acetic acid ethyl ester	Sol. in $CHCl_3$	218
5.80	1724	s	acid C=O	phenacetamidoallylmalonic acid	S	151
		s	acid C=O	2-benzyl-Δ^2-thiazoline-4-carboxylic acid hydrochloride	S	211
		s	acid C=O	acetic acid	L	103

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
5.80	1724	s	acid C=O	phenaceturic acid	S	135
		s	acid C=O	*dl*-glutamic acid hydrochloride	S	227
		m	acid C=O	succinic acid	S	105
		s	joint ester-amide C=O	N-methoxy-N-methylurethane	L	158
		s	ester C=O (double)	diethyl phenacetamidosuccinate	S	131
		s	ester C=O (conjugated)	methyl α-acetamido-β,β-dimethylacrylate	S	128
		s	unassigned	2-methylbenzoxazole	L	214
		s	acid C=O	caprylic acid	L	106
5.81	1721	s	acid C=O	thioacetic acid	L	103
		m	acid C=O	monoethyl phenacetamidomalonate	S	130
		s	acid C=O	α-phenacetamidoisobutyric acid	S	139
		s	acid C=O	α-phenacetamido-β,β-dimethoxypropionic acid	S	127
		m	ester C=O	sodium ethyl phenacetamidomalonate	S	115
		s	keto C=O	methyl ethyl ketone	L	166
		s	joint ester-amide C=O	ethyl carbazate	S	160
		w	aldehyde C=O	phenacetamidoacetaldehyde	S	148
		m	carboxylic ester C=O (conjugated)	2-benzyl-4-carbethoxy-imidazole-1-acetic acid ethyl ester	S	218
		s	ester C=O (conjugated)	methyl α-benzamido-β,β-dimethylacrylate	S	138
		s	4 C=O ring	2-thiohydantoin	S	175
		s	lactone C=O	dehydracetic acid	S	231
		s	C=O (diketo)	biacetyl	L	167
5.82	1718	s	4 C=O	1-benzyl-5,6-dihydrouracil	S	180
		s	4 C=O	uracil	S	176
		s	4 C=O	5,6-dihydro-2-thiouracil	S	179
		s	4 C=O	5-furfurylidene-2-thiohydantoin	S	178
		m	acid C=O	α-phenacetamido-n-valeric acid	S	134
		s	acid C=O	formic acid	L	103
		m	acid C=O	α-phenacetamido-n-caproic acid	S	138
		s	joint ester amide C=O	N-hydroxyurethane	L	158
		s	N-acyl C=O	1-acetyl-2-thiohydantoin	S	177
		w	unassigned	acetylthiourea	S	170
5.83	1715	s	acid C=O	*dl*-N-phenacetyl-β-phenylalanine	S	143
		s	acid C=O	*dl*-N-phenacetylalanine	S	141
		m	acid C=O	*l*-N-phenacetylproline	S	153
		s	acid C=O	N-acetylthiazolidine-4-carboxylic acid	S	154
		s	acid C=O	N-phenacetyl-N-methylanthranilic acid	S	154
5.84	1712	s	joint ester amide C=O	N-carbethoxybenzalhydrazone	S	159
		s	2 C=O	allantoin	S	174
		s	aldehyde C=O (conjugated)	benzaldehyde	L	168
		s	2 C=O	1-methylhydantoin	S	174

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
5.84	1712	s	1 acyl C=O	1-phenacetyl-5-(N-benzylacetamido-methyl)-2-thiohydantoin	S	175
		s	acid C=O	α-acetamidoisobutyric acid	S	146
5.85	1709	s	acid C=O	N-phenacetylsarcosine	S	156
5.86	1706	s	ester C=O (conjugated)	ethyl-α-amino-β,β-dimethylacrylate	S	109
		m	keto C=O ester C=O (conjugated?)	α-phenylazoacetoacetic acid ethyl ester	S	231
		s	ester C=O (conjugated)	acetylurethane (enol form)	L	159
		s	acid C=O	*dl*-N-phenacetylvaline	S	144
		m	acid C=O	α-phenacetamido-α-methyl-n-butyric acid	S	140
		s	acid C=O	N-thiocarbamyl-β-benzyl-aminopropionic acid	S	105
		s	2 C=O	N-(n-amyl)-succinimide	L	172
		s	joint ester-amide C=O	N-methylurethane	L	158
		s	2 C=O	3-methylhydantoin	S	175
5.87	1703	s	4 C=O	rhodanine	S	189
		s	acid C=O	phenylacetic acid	S	106
5.88	1700	s	acid C=O	δ-amino-n-valeric acid hydrochloride	S	228
		s	keto C=O	phenacyl acetate	S	107
		s	lactam C=O	γ-butyrolactam	L	162
		s	unassigned	xanthine	S	209
		s	C=O	1-ethyloxindole-2	S	224
5.89	1697	s	acid C=O	*d*-N-phenacetylisoleucine	S	142
		s	acid C=O	ϵ-benzamidocaproic acid	S	136
		s	2 C=O	barbituric acid	S	181
		s	2 C=O	alloxan (monohydrate)	S	172
		s	ester C=O (conjugated)	Δ^2-pyrazoline-3,4-dicarboxylic acid dimethyl ester	S	225
		s	C=N	N-carbethoxybenzalhydrazone	S	159
		s	acid C=O (conjugated)	α-acetamido-β,β-dimethylacrylic acid	S	127
		s	2 C=O	hydantoin	S	173
5.90	1694	s	acid C=O (dicarboxylic)	glutaric acid	S	104
		s	acid C=O	succinic acid	S	105
		s	acid C=O	α-benzamido-β,β-dimethylacrylic acid	S	138
		s	acid C=O	δ-phenacetamido-n-valeric acid	S	132
		s	acid C=O	ϵ-phenacetamido-n-caproic acid	S	131
		s	2 C=O	succinimide	S	171
		s	2 C=O	5,6-dihydrouracil	S	179
		s	2 C=O	5-methylhydantoin	S	173
		s	4 C=O	6-phenyl-5,6-dihydro-2-thiouracil	S	180
		s	amide I	acetamide	S	125
		s	N-acyl C=O	1-benzoyl-2-thiohydantoin	S	177
		s	$C{=}NH_2^+$	phenaceturiminomethylether hydrochloride	S	184
		s	amide I	cyanoacetamide	S	126

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
5.90	1694	s	amide I	benzyl carbamate	S	127
5.91	1691	w	urea C=O	phenacetylurea	S	169
		m	unassigned	methyl guanidine sulphate	S	187
		s	unassigned	benzoxazole	L	215
5.92	1689	s	acid C=O (conjugated)	p-nitrobenzoic acid	S	104
		w	acid C=O	*dl*-aspartic acid	S	121
		s	ester C=O (conjugated)	methyl anthranilate	L	107
		m	N-acyl C=O	acetylthiourea	S	170
		s	keto C=O (conjugated)	acetophenone	L	166
		s	unassigned	urea	S	169
5.93	1686	s	acid C=O (conjugated)	N-phenacetylanthranilic acid	S	129
		s	acid C=O	N-phenacetyl-β-alanine	S	133
		s	4 C=O	5-phenacetamido-2-thiouracil	S	180
		s	ester C=O (conjugated)	methyl N-phenacetylanthranilate	L	129
5.94	1683	s	acid C=O (conjugated)	benzoic acid	S	104
		m	C=N	acetoxime	S	182
5.95	1680	s	4 C=O	5-(p-dimethylaminobenzal)-rhodanine	S	189
		m	unassigned	ϵ-amino-n-caproic acid	S	120
5.96	1677	s	amide I	phenacetamide	Sol.	125
5.97	1674	s	C=N (ring)	2-phenyl-4-isopropylidene-oxazolone-5	S	161
5.98	1671	s	N-acyl C=O (conjugated)	N-benzoyl-N-methoxyurethane	L	158
		s	amide I	N-methylformamide	L	146
		s	N-acyl C=O	1-phenacetyl-5,5-dimethyl-2-thiohydantoin	S	174
		s	acid C=O	*dl*-glutamic acid hydrochloride	S	227
5.99	1669	s	4 C=O	creatinine	S	230
		s	keto C=O	2,6-dimethyl pyrone	S	165
		s	ring C=N	2-benzyl-4,4-dimethyloxazolone-5	S	161
		s	amide I	N-phenacetylanthranilic acid	S	129
		s	amide I	1-benzyl-5-phenacetamido-5,6-dihydro-2-thiouracil	S	179
6.00	1666	s	amide I	formanilide	S	148
		w	amide I	silver phenaceturate hydrate	S	119
		w	amide I	sodium ethyl phenacetamidomalonate	S	115
		s	amide I	N-chloro-N-methylbenzamide	L	67
		s	N-acyl C=O	N-phenacetyl-N-phenylglycine methyl ester	L	155
		s	acid C=O (conjugated)	anthranilic acid	S	121
		s	2 C=O	1-benzyl-5,6-dihydrouracil	S	180
		s, s	urea C=O, N-acyl C=O	acetyl urea	S	169
		s	N-acyl C=O	phenacetyl urea	S	169
		s	amide I, 4 C=O	1-benzyl-5-phenacetamido-2-thiouracil	S	178
		s	C=N	methyl-N-phenylbenzamidate	L	183
		s	amide I	ethyl phenaceturate	Sol'n	137
6.01	1663	s	amide I	*dl*-N-phenacetyl-β-phenylalanine	S	143
		s	amide I	phenacetamidomalonic acid	S	130

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.01	1663	s	keto C=O (conjugated)	quinone	S	165
		s	2 C=O	uracil	S	176
		s	unassigned	xanthine	S	209
		s	amide I	benzamide	S	126
6.02	1661	s	amide I	allantoin	S	174
		s	joint ester, amide C=O	urethane	S	157
		w	C=C	α-acetamido-β,β-dimethylacrylic acid	S	127
		m	unassigned	2-aminobenzimidazole	S	216
		s	acid C=O (conjugated)	salicylic acid	S	105
6.03	1658	w	C=C	3,5-dimethylpyrazole	S	223
		s	amide I	*dl*-N-phenacetyl-β-phenylalanine methyl ester	S	144
		s	acid C=O (conjugated)	N-methylanthranilic acid	S	121
		w	unassigned	methyl δ-phenacetamido-n-valerate	S	132
		s	ring C=N	4-isopropyl-2-phenyloxazolone-5	S	162
		s	2 C=O	2,4-dioxythiazolidine	S	211
		m	δNH_3^+	*dl*-α-amino-n-caproic acid	S	120
		s	amide I	ϵ-phenylcaproamide	S	126
		s	N-acyl C=O	N-acetyl thiazolidine-4-carboxylic acid methyl ester	Sol. in $CHCl_3$	109
6.04	1655	w	amide I	sodium phenaceturate hydrate	S	116
		s	amide I	methyl α-phenacetamido-β,β-dimethoxy-propionate	L	128
		s	amide I	phenacetylsarcosine methyl ester	L	156
		m	ring C=N	4-methoxybenzyl-2-phenyloxazolone-5	S	162
		s	N-acyl C=O	1-phenacetyl-5(N-benzylacetamido-methyl)-2-thiohydantoin	S	175
		w	unassigned	*dl*-α-amino-n-valeric acid	S	120
		s	amide I, δNH_2	propionamide	S	126
6.05	1653	s	amide I	N-phenacetyl-β-alanine methyl ester	L	133
		s	amide I	N-methylphenacetamide	S	146
		s	amide I	benzanilide	S	147
		s	amide I	ethyl phenaceturate	S	137
		s	NH_2 amide type C=O	hydantoic amide	S	171
		s	unassigned	guanidine thiocyanate	S	186
		s	N-acyl C=O	N-acetylthiazolidine-4-carboxylic acid methyl ester	L	109
6.06	1650	s	amide I	ethyl hydantoate	S	110
		s	amide I	phenaceturiminomethylether hydrochloride	S	184
		s	carboxylate ion	sodium ethyl phenacetamidomalonate	S	115
		s	N-acyl C=O	sodium N-acetylthiazolidine-4-carboxylate hydrate	S	114
		w	unassigned	ϵ-amino-n-caproic acid	S	120
		w	unassigned	β-alanine	S	123
6.07	1647	m	amide I	barium phenaceturate hexahydrate	S	118

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.07	1647	s	amide I	*dl*-N-phenacetylvaline methyl ester	L	145
		s	amide I	methyl ϵ-benzamidocaproate	L	137
		s	ring C=N	4-isobutyl-2-phenyloxazolone-5	S	162
		s	C=N	N,N′-dimethyl-N-benzoylbenzamidine	S	157
		m	C=C	5-(*o*-hydroxybenzal)-2-thiohydantoin	S	177
		m	unassigned	2-aminobenzothiazole	S	213
		s, s	amide I and $-C(-O-CH_3)=NH$	phenaceturiminomethylether	S	182
6.08	1645	s	amide I	*dl*-N-phenacetylalanine	S	141
		s	amide I	N-p-nitrobenzamidopiperidine	S	150
		m	amide I, C=C	methyl α-acetamido-β,β-dimethyl-acrylate	S	128
		s	amide I	phenacetamidoacetaldehyde	S	148
		s	amide I	N-ethylacetamide	L	147
		s	δNH_2 / amide I	phenacetamide	S	125
		s	amide I	*dl*-N-phenacetyl-alanine methyl ester	S	142
		s	N-acyl C=O	*l*-N-phenacetyl-proline methyl ester	L	157
		m	ring C=N	2-phenyl-4-benzyl-oxazolone-5	S	161
		w	δNH_2 (?)	ethyl carbazate	S	160
		m	C=C	5-benzal-2-thiohydantoin	S	176
		s	unassigned	sarcosine	S	122
		s	unassigned	methylguanidine sulphate	S	187
6.09	1642	s	amide I	methyl α-phenacetamidoisobutyrate	S	140
		m	amide I	sodium-ϵ-benzamido-n-caproate	S	115
		s	amide I, C=C	α-benzamido-β,β-dimethylacrylic acid	S	138
		s	amide I	ethyl hippurate	S	135
		s	amide I	N-ethylphenacetamide	S	149
		m	amide I	N-methylbenzamide	S	149
		s	ring C=N	5-furfurylidene-2-thiohydantoin	S	178
		s	amide I	methyl α-phenacetamido-n-caproate	L	139
		s	unassigned	dehydracetic acid	S	231
		s	carboxylate ion, δNH_3^+	*d*-glutamic acid	S	123
6.10	1639	w	amide I	barium phenaceturate (anhydrous)	S	118
		w	amide I	ethyl α-allylphenaceturate	S	110
		m	amide I	diethyl phenacetamidosuccinate	S	131
		s	amide I	methyl phenaceturate	S	136
		s	amide I	methyl α-benzamido-β,β-dimethyl-acrylate	S	138
		s	amide I	N-phenacetyl-β-alanine	S	133
		s	amide I	*d*-N-phenacetylisoleucine methyl ester	S	143
		s	amide I	5-phenacetamido-2-thiouracil	S	180
		s	amide I	2,4,6-trimethylphenaceturic acid methyl ester	S	145
		s	amide I	methyl α-phenacetimido-α-methyl butyrate	S	141

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.10	1639	m	amide I	methyl α-phenacetamido-n-valerate	S	134
		s	amide I	N-benzamidopiperidine	S	150
		s	amide I	N,N-diethyl acetamide	L	151
6.11	1637	s	amide I	δ-phenacetamido-n-valeric acid	S	132
		s	amide I	ϵ-phenacetamido-n-caproic acid	S	131
		s	amide I	N-benzyl formamide	S	148
		w	conjugated C=C	ethoxymethylenemalonic ester	L	108
		w	conjugated C=C	ethyl α-amino-β,β-dimethylacrylate	L	109
		s	N-acyl C=O	N-phenacetyl-N-phenylglycine	S	155
		s	δNH_3^+	α-aminoisobutyric acid	S	119
		s	N-acyl C=O	acetyl piperidine	L	153
		m	δNH_3^+	*dl*-valine	S	119
6.12	1634	s	amide I	δ-phenacetamido-n-valeric acid methyl ester	S	132
		s	amide I	N,N-dimethylbenzamide	L	152
		s	amide I	N,N-dimethylphenacetamide	S	152
		m	unassigned	2-ethylmercaptobenzoxazole	L	215
		m	thiazole I	2-amino-4-(p-biphenyl)thiazole	S	210
		s	δHOH	sodium N-acetylthiazolidine-4-carboxylate hydrate	S	114
		w	δNH_2	acetamide	S	125
		m	δNH_2	benzamide	S	126
		m	unassigned	urea	S	169
		m	δNH_2	acetyl urea	S	169
		m	δNH_2	phenacetyl urea	S	169
		m	carboxylate ion	*dl*-α-amino-α-methylbutyric acid	Sol.	120
6.13	1631	m	δNH_3^+	β-alanine	S	123
		w	δNH_3^+	ϵ-amino-n-caproic acid	S	120
		s	amide I	sodium salt of *dl*-N-phenacetylalanine	S	116
		s	N-acyl C=O	N,N′-dimethyl-N-benzoylbenzamidine	S	157
		m	δHOH	silver phenaceturate hydrate	S	119
		s	amide I, δHOH	sodium hippurate hydrate	S	116
6.14	1629	w	amide I	ϵ-benzamidecaproic acid	S	136
		w	δNH_2	ϵ-phenyl caproamide	S	126
		m	δNH_2	benzyl carbamate	S	127
6.15	1626	s	thiazole I	2-aminothiazole	S	210
		w	N=N	α-phenylazoacetoacetic acid ethyl ester	S	231
		m	δNH_2	N-thiocarbamyl-β-benzylaminopropionic acid	S	105
		s	amide I	N-phenacetyl-N-methylanthranilic acid	S	154
6.15	1626	s	amide I	N acetyl thiazolidine 4 carboxylic acid	S	154
6.16	1623	s, s	amide I, carboxylate ion	sodium phenacetylsarcosinate	S	117
		w	δNH_3^+	*dl*-α-amino-n-valeric acid	S	120
		m	δNH_3^+	*dl*-β-phenylalanine	S	123
		s	unassigned	2-methylbenzoxazole	L	214
		m	thiazole I	2-mercapto-4,5-dimethylthiazole	S	210

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.17	1621	s	amide I	*dl*-N-phenacetylvaline	S	144
		m	δNH_3^+	cystine	S	121
		m	δNH_3^+	*dl*-alanine	S	119
		s	unassigned	3-methyl-pyrazolone-5	S	222
		s	carboxylate ion	*l*-proline	S	122
		m	ring C=N	methyl-2-benzylthiazoline-Δ^2-4-carboxylate	L	108
		w	δHOH	barium phenaceturatehexahydrate	S	118
6.18	1618	s	amide I	α-acetamido-β,β-dimethylacrylic acid	S	127
		s	amide I	*d*-N-phenacetylisoleucine	S	142
		s	amide I	sym-diethylurea	S	170
		m	amide I	α-acetamidoisobutyric acid	S	146
		s	δNH_3^+	*dl*-α-amino-α-methyl-n-butyric acid	Sol.	120
		s	amide I	α-phenacetamido-β,β-dimethoxypropionic acid	S	127
		s	δNH_2	urethane	S	157
		w, s	δNH_3^+, carboxylate ion	*dl*-aspartic acid	S	121
		w	δNH_2	anthranilic acid	S	121
		m	δNH_2	cyanoacetamide	S	126
6.19	1615	s	carboxylate ion	sarcosine	S	122
		s	δHOH	sodium phenaceturate hydrate	S	116
6.20	1613	s	amide I	phenacetamidoallylmalonic acid	S	151
		w	amide I	monoethyl phenacetamidomalonate	S	130
		s	amide I	α-phenacetamidoisobutyric acid	S	139
		s	unassigned	thiourea	S	170
		s	δNH_2	anhydrous hydrazine	L	160
		m	ring	1-ethyloxindole-2	S	224
		m, m	δNH_2, phenyl	methyl anthranilate	S	107
		m, m	δNH_3^+, phenyl	*l*-tyrosine	S	123
		s	unassigned	hydantoic amide	S	171
		w	δNH_3^+	*dl*-glutamic acid hydrochloride	S	227
6.21	1610	m	δNH_3^+	*d*-isoleucine	S	121
		s	δNH_3^+	ethylamine hydrochloride	S	229
		w	δNH_3^+	α-aminoisobutyric acid hydrochloride	S	226
		w	δNH_2	ethyl α-amino-β,β-dimethylacrylate	L	109
		s	unassigned	urea	S	169
		s	ring vibration	2,6-dimethylpyrone	S	165
		s, m	carboxylate ion, δNH_3^+	α-amino-α-methyl-n-butyric acid	S	120
6.22	1608	s	amide I	α-phenacetamido-α-methyl-n-butyric acid	S	140
		s	amide I	phenaceturic acid	S	135
		w	δNH_3^+	*dl*-alanine hydrochloride	S	226
		w	conjugated C=N	acetylurethane (enol form)	L	159
		w	δNH_3^+, phenyl	*dl*-β-phenylalanine hydrochloride	S	228
		w	unassigned	2-ethylmercaptobenzoxazole	L	215

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.23	1605	s	C=N, phenyl	2-phenylthiazoline-Δ^2	L	211
6.24	1603	s	amide I	N-phenacetylsarcosine	S	156
		w	δNH_2	allantoin	S	174
		s	unassigned	1-methyl-2,4-dioxo-3-phenylpyrrolidine	S	224
6.25	1601	m	phenyl	N-phenylglycine hydrochloride	S	228
		s	amide I	α-phenacetamido-n-valeric acid	S	134
		m	δNH_2	acetyl thiourea	S	170
		s	amide I	α-phenacetamido-n-caproic acid	S	138
		s	unassigned	benzoxazole	L	215
6.26	1598	s	carboxylate ion	*dl*-valine	S	119
		w	ring vibration	pyridine	L	225
		s	amide I	hippuric acid	S	135
6.27	1595	s	C=N	3,5-dimethylpyrazole	S	223
		w	ring vibration	5,6-dimethylpyrone	S	165
		s	carboxylate ion	sodium hippurate hydrate	S	116
		s	amide I	1,2-diacetyl hydrazine	S	160
6.28	1592	w	δNH_3^+	α-amino-α-methylbutyric acid hydrochloride	S	226
		w	δNH_2^+	*l*-proline hydrochloride	S	228
		w	C=C	quinone	S	165
		w	δNH_3^+	*dl*-α-amino-n-caproic acid hydrochloride	S	227
		s	δNH_3^+	*l*-tyrosine hydrochloride	S	229
		m	δNH_2	ethanolamine (in $CHCl_3$)	Sol.	193
6.29	1590	s	carboxylate ion	*dl*-alanine	S	119
		s	carboxylate ion	*dl*-β-phenylalanine	S	123
		s	carboxylate ion	sodium N-acetylthiazolidine-4-carboxylate hydrate	S	114
		s	N-acyl C=O	*l*-N-phenacetylproline	S	153
		w	δNH_3^+	cystine hydrochloride	S	227
		m	δNH_3^+	δ-amino-n-valeric acid hydrochloride	S	228
		s	N-acyl C=O	N-acetylthiazolidine-4-carboxylic acid	S	154
		s	N-acyl C=O	N-phenacetyl-N-methyl-anthranilic acid	S	154
		m	ring C=N	2-benzyl-Δ^2-thiazoline-4-carboxylic acid	S	211
		s	unassigned	sym-diethylurea	S	170
		w	unassigned	creatinine	S	230
		m	unassigned	2-mercapto-4-phenylthiazole	S	210
		s	C=N	2-benzylimidazoline	S	222
6.30	1587	s	carboxylate ion	*dl*-α-amino-n-caproic acid	S	120
		s	carboxylate ion	sodium phenaceturate hydrate	S	116
		s	thioureide ion	5,6-dihydro-2-thiouracil	S	179
		s	carboxylate ion	cystine	S	121
		s	unassigned (NH_2?)	ethyl hydantoate	S	110
6.31	1585	s	carboxylate ion	*d*-isoleucine	S	121
		s	carboxylate ion	*l*-tyrosine	S	123
		w	δNH_3^+	*dl*-α-amino-n-valeric acid hydrochloride	S	227

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.31	1585	m	unassigned	2-ethylmercaptobenzoxazole	L	215
		m	amide I	methyl N-phenacetylanthranilate	L	129
		m	unassigned	6-amino-2-mercaptobenzothiazole	S	214
6.32	1582	s	carboxylate ion	sodium salt of *dl*-N-phenacetylalanine	S	116
		s	carboxylate ion	*dl*-α-amino-n-valeric acid	S	120
		m	anilino	N-methylanthranilic acid	S	121
		s	thioureide ion	6-phenyl-5,6-dihydro-2-thiouracil	S	180
		s	C═N, C═C	2-benzylimidazole-Δ^1	S	217
6.33	1580	s	carboxylate ion	α-aminoisobutyric acid	S	119
		s	carboxylate ion	sodium acetate	L	114
		s	thioureide ion	5-phenacetamido-2-thiouracil	S	180
		s	ring C═N	pyridine	L	225
		s	unassigned	2-methylbenzoxazole	L	214
6.34	1577	s	carboxylate ion, anilino	N-phenylglycine potassium salt	S	115
		m	carboxylate ion	silver phenaceturate hydrate	S	119
		w	unassigned	*dl*-alanine hydrochloride	S	226
		s	carboxylate ion	sodium acetate (methanol)	Sol.	114
6.35	1575	s	carboxylate ion	barium phenaceturate (anhydrous)	S	118
		s	δNH_3^+	cysteine hydrochloride	S	227
6.36	1572	m	amide II	N-benzamidopiperidine	S	150
6.37	1570	m	thiazole I	2-mercapto-4-phenylthiazole	S	210
		w	δNH_3^+	cystine hydrochloride	S	227
6.38	1567	s	carboxylate ion	β-alanine	S	123
		s	carboxylate ion	ϵ-amino-n-caproic acid	S	120
		s	carboxylate ion	N-phenylglycine	S	122
		s	thioureide ion	5-(p-dimethylaminobenzal)-rhodanine	S	189
		s	unassigned	2-aminobenzimidazole	S	216
		s	carboxylate ion	sodium-ϵ-benzamido-n-caproate	S	115
6.39	1565	w	unassigned	xanthine	S	209
		s	amide II	N-methylphenacetamide	S	146
		m	amide II	α-phenacetamide-β,β-dimethoxypropionic acid	S	127
6.40	1563	s	amide II	N-ethylphenacetamide	S	149
		s	amide II, carboxylate ion	barium phenaceturate hexahydrate	S	118
		w	unassigned	*l*-proline	S	122
		s	amide II	ethyl phenaceturate	S	137
		m	C═N	2-benzyl-4-carbethoxyimidazoline-1-acetic acid ethyl ester	Sat. Sol. in $CHCl_3$	218
6.41	1560	s	amide II	N-carbethoxybenzalhydrazone	S	159
		s	amide II	methyl δ-phenacetamido-n-valerate	S	132
		m	amide II	phenacetamidoacetaldehyde	S	148
		w	unassigned	2-methylbenzothiazole	L	213
		w	anilino	N-phenylglycine hydrochloride	S	228
6.42	1558	m	amide II	N-ethylacetamide	L	147
		s	amide II	*d*-N-phenacetylisoleucine methyl ester	S	143
6.43	1555	m	amide II	phenaceturiminomethylether	S	182

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.43	1555	s	amide II	hippuric acid	S	135
		s	amide II	methyl phenaceturate	S	136
		s	amide II	silver phenaceturate hydrate	S	119
		m	amide II	methyl α-phenacetamido-α-methyl butyrate	S	141
		m	amide II	*dl*-N-phenacetylvaline	S	144
		s	amide II	methyl α-phenacetamido-n-valerate	S	134
		s	NO_2	nitromethane	L	190
		s	unassigned	thiazolidine-4-carboxylic methyl ester hydrochloride	S	108
		m	unassigned	3-methyl-5-pyrazolone	S	222
		s	amide II	sodium hippurate hydrate	S	116
6.44	1553	s	amide II	N-methylbenzamide	S	149
		s	amide II	*dl*-N-phenacetylalanine methyl ester	S	142
		s	thioureide ion	5-methyl-2-thiohydantoin	S	177
		w	δNH_2^+	2,2-dimethylthiazolidine-4-carboxylic acid hydrochloride	S	212
6.45	1550	s	amide II	ethyl hydantoate	S	110
		s	amide II	*d*-N-phenacetylisoleucine	S	142
		s	amide II	2,4,6-trimethylphenaceturic acid methyl ester	S	145
		s	amide II	formanilide	S	148
6.46	1548	s	amide II	δ-phenacetamido-n-valeric acid	S	132
		m	amide II	methyl α-phenacetamidoisobutyrate	S	140
		s	unassigned	dehydracetic acid	S	231
		m	amide II	α-phenacetamido-n-valeric acid	S	134
		w	NO_2	N-p-nitrobenzamidopiperidine	S	150
		s	amide II	sodium ϵ-benzamidocaproate	S	115
6.47	1546	s	amide II	*dl*-N-phenacetylalanine	S	141
		s	amino acid II	α-aminoisobutyric acid	S	119
		s	amide II	N-methyl formamide	S	146
		s	C=N	2-benzyl-4-carbethoxyimidazole-1-acetic acid ethyl ester	S	218
6.48	1543	m	amide II	N-methylurethane	L	158
		m	amide II	*dl*-N-phenacetyl-β-phenylalanine methyl ester	S	144
		s	amide II	α-acetamidoisobutyric acid	S	146
		m	amide II	N-phenacetyl-β-alanine	S	133
		w	amide II	N-phenacetyl-β-alanine methyl ester	L	133
		w	ring	pentachlorophenol	S	192
		s	thioureide ion	acetylthiourea	S	170
6.49	1541	m	amide II	methyl α-phenacetamido-β,β-dimethoxypropionate	L	128
		s	amide II	methyl ϵ-benzamidocaproate	L	137
		m	NO_2	p-nitrobenzoic acid	S	104
6.50	1538	w	amide II	phenaceturiminomethylether hydrochloride	S	184

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.50	1538	s	amide II	α-acetamido-β,β-dimethylacrylic acid	S	127
		m	amide II	phenacetamidomalonic acid	S	130
		s	amide II	1-benzyl-5-phenacetamido-2-thiouracil	S	178
		w	amide II	sodium salt of *dl*-N-phenacetylalanine	S	116
		s	thiazole II	2-amino-4-(p-diphenyl)thiazole	S	210
		w	amide II	barium phenaceturate (anhydrous)	S	118
		m	amide II	*dl*-N-phenacetylvaline methyl ester	L	145
		m	amide II	methyl α-phenacetamido-n-caproate	L	139
		w	amide II	diethyl thiophenacetamidomalonate	S	111
		m	ring C=N (conjugated)	Δ^2-pyrazoline-3,4-dicarboxylic acid dimethyl ester	S	225
		s	thioureide ion	1-benzyl-5,6-dihydro-2-thiouracil	S	178
6.51	1536	s	amide II	5-phenacetamido-2-thiouracil	S	180
		w	amide II	N-benzylformamide	S	148
		s	amide II	α-phenacetamidoisobutyric acid	S	139
		s	amide II	hydantoic amide	S	171
		s	amino acid II	ϵ-amino-n-caproic acid	S	120
6.52	1534	s	amide II	allantoin	S	174
		s	amide II	ϵ-benzamidocaproic acid	S	136
		s	amide II	monoethyl phenacetamidomalonate	S	130
		s	amide II	α-phenacetamido-n-caproic acid	S	138
		s	amide II	methyl α-acetamido-β,β-dimethyl-acrylate	S	128
		s	amide II	benzanilide	S	147
		m	thioureide ion	2-thiohydantoin	S	175
		m	amide II	1,2-diacetylhydrazine	S	160
		s	amide II, thioureide ion	1-benzyl-5-phenacetamido-5,6-dihydro-2-thiouracil	S	179
6.53	1532	s	amide II	ϵ-phenacetamido-n-caproic acid	S	131
		w	amide II	N-phenacetylanthranilic acid	S	129
6.54	1530	s	amide II	ethyl hippurate	S	135
		s	amide II	phenaceturic acid	S	135
		s	unassigned	2-aminobenzothiazole	S	213
		s	amide II	ethyl phenaceturate (in $CHCl_3$)	Sol.	137
6.55	1527	s	amide II	ethyl α-allylphenaceturate	S	110
		s	amide II	α-phenacetamido-α-methyl-n-butyric acid	S	140
		s	unassigned	2-methylbenzothiazole	L	213
6.56	1525	m	amide II	sodium ethyl phenacetamidomalonate	S	115
		w	amino acid II	dl-α-amino-α-methylbutyric acid	S	120
		s	NO_2	p-nitrotoluene	S	190
6.57	1522	m	amide II	diethylphenacetamidosuccinate	S	131
		w	amino acid II	*dl*-alanine	S	119
		s	amino acid hydrochloride II	α-aminoisobutyric acid hydrochloride	S	226
		s	anilino	5-(p-dimethylaminobenzal)-rhodanine	S	189
		s	unassigned	benzoxazole	L	215

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.58	1520	m	amide II	*dl*-N-phenacetyl-β-phenylalanine	S	143
		w	amino acid II	*dl*-α-amino-n-caproic acid	S	120
		m	amide II	methyl N-phenacetyl anthranilate	L	129
6.59	1518	m	amide II	N-p-nitrobenzamidopiperidine	S	150
		w	amino acid hydrochloride II	cysteine hydrochloride	S	227
		w	anilino	N-phenylglycine ethyl ester	S	108
6.60	1516	s	amide II	methyl α-benzamido-β,β-dimethyl acrylate	S	138
		s	amide II	phenacetamidoallylmalonic acid	S	151
		w	amide II	sodium phenaceturate hydrate	S	116
		w	amino acid II	*dl*-α-amino-n-valeric acid	S	120
		s	thioureide ion	2-thiothiazolidone	S	189
		s	amino acid hydrochloride II	*l*-tyrosine hydrochloride	S	229
		s	amino acid II	*d*-glutamic acid	S	123
		s	thiazole II	2-aminothiazole	S	210
		s	amino acid hydrochloride II	α-amino-α-methylbutyric acid hydrochloride	S	226
6.61	1513	m	amide II	ethyl carbazate	S	160
		s	amino acid II	*d*-isoleucine	S	121
		s	thioureide ion	N-thiocarbamyl-β-benzylaminopropionic acid	S	105
6.62	1511	w	unassigned	2-phenylbenzothiazole	S	212
		s	unassigned	2-mercapto-6-amino-benzothiazole	S	214
		s	C=C	α-phenazoacetoacetic acid ethyl ester	S	231
		w	anilino	deutero N-phenyl-glycine ethyl ester	S	108
6.63	1509	s	amide II	α-benzamido-β,β-dimethyl acrylic acid	S	138
		s	amino acid hydrochloride II	*dl*-glutamic acid hydrochloride	S	227
6.65	1504	s	amino acid II	*dl*-β-phenylalanine	S	123
		s	amino acid II	*dl*-valine	S	119
6.66	1502	s	amino acid hydrochloride II	cystine hydrochloride	S	227
		s	amino acid hydrochloride II	*dl*-alanine hydrochloride	S	226
		s	amino acid II	β-alanine	S	123
		s	ring	N-benzylpyrrole	L	223
		s	unassigned	acetoxime	S	182
6.67	1499	s	amide II	creatinine	S	230
		s	amino acid II	*dl*-aspartic acid	S	121
		s	unassigned	2-ethylmercaptobenzoxazole	L	215
		s	anilino	N-phenylglycine potassium salt	S	115
6.68	1497	w	amino acid hydrochloride II	*dl*-α-amino-n-valeric acid hydrochloride	S	227
6.69	1494	s	amino acid hydrochloride II	α-amino-α-methylbutyric acid hydrochloride	S	226
		s	unassigned	2-mercaptobenzothiazole	S	213
		m	ring	1-ethyloxindole-2	S	224
6.70	1492	s	thiazole II	2-mercapto-4-phenylthiazole	S	210
		s	thioureide ion	1-benzyl-5-phenacetamido-2-thiouracil	S	178
		s	amino acid hydrochloride II	*dl*-α-amino-n-caproic acid hydrochloride	S	227

TABLE 2. CATALOGUE OF ABSORPTION ASSIGNMENTS IN THE 6 μ REGION (*Continued*)

λ	$\bar{\nu}$	I	Assignment	Name of Compound	State	Spectrum Page No.
6.72	1488	s	thioureide ion	5-(*o*-hydroxybenzal)-2-thiohydantoin	S	177
6.73	1485	s	thioureide ion	5-benzal-2-thiohydantoin	S	176
6.74	1483	m	thioureide ion	5-furfurylidene-2-thiohydantoin	S	178
		s	amino acid hydrochloride II	*dl*-β-phenylalanine hydrochloride	S	228
		m	ring	pyridine	L	225
6.76	1479	s	unassigned	2-phenylbenzothiazole	S	212
		s	thiazole II	2-mercapto-4,5-dimethyl thiazole	S	210
6.79	1473	s	thioureide ion	1-phenacetyl-5(N-benzylacetamido methyl)-2-thiohydantoin	S	175
		s	unassigned	benzothiazole	L	212
6.80	1471	m	thioureide ion	1-acetyl-2-thiohydantoin	S	177
6.81	1460	s	thioureide ion	1-phenacetyl-2-thio-5,5-dimethyl-hydantoin	S	174
6.87	1456	s	thioureide ion	1-benzoyl-2-thiohydantoin	S	177
6.92	1446	s	thioureide ion	rhodanine	S	189

Chapter IV

A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES

Introduction

Exact theoretical assignments must serve as a point of departure in any empirical investigations, and in the following tables an effort has been made to summarize all such existing information for the convenience of the analyst. For this purpose a comparison study of 135 simple molecules was conducted, and the results are tabulated in a manner similar to that in Chapter III. References listed in Herzberg's *Infrared and Raman Spectra of Polyatomic Molecules* [9] were used. These references relate to some 350 molecules containing from three to twelve atoms. Of these, Herzberg discusses 60 in some detail. With the aid of the references, the literature was searched to discover which of the other molecules had been analyzed. Theoretical assignments were found for about a third of the citations, but of these only half were analyzed to any degree of completeness, the other half having only a few strong bands assigned.

It should be emphasized that the catalogue in this chapter is not the result of a critical study of the interpretations offered. No attempt was made to evaluate the assignments given by the references cited as long as they were unchallenged by others. In some cases, where two references disagreed on interpretation, a choice was made based on the completeness of the research and usually favoring the more recent analysis. In a few cases, the choice seemed difficult and both assignments were recorded in the catalogue as alternatives. Assignments based on infrared data were favored whenever available. However, the compilation had to draw heavily from Raman work as will be seen from a glance at the wavelength catalogue.

[9] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Co., New York, 1945.

No claim is made for completeness in this survey, yet it is felt to be sufficient for the intended purpose of orientation. In all, 135 molecules are to be found in the catalogue. They are listed alphabetically, together with references, in Table 3. Two catalogues have been compiled in order to present this information on simple molecules on the same basis as for the specialized data in Chapter III. Table 4 is a summary of the wavelength ranges within which the various assignments fall. Table 5 is the complete wavelength catalogue upon which Table 4 is based.

Function of Different Spectral Regions in Structural Analysis

A study of these catalogues will serve to emphasize the different purposes which different regions of the spectrum serve in structural analysis. In the short wavelength region (around 3 μ) the location of certain absorptions is definite evidence of the presence of hydrogen bonds in the molecule such as are found in CH, OH and NH groups. The position of these absorption bands is, moreover, very insensitive to changes of the molecular skeleton.

The long wavelength region (beyond 8 μ) is quite the opposite. In this region, the absorption bands form a "profile" which is more characteristic of the molecules as a whole. Even changes in structure which are minor from the chemist's viewpoint will cause major changes in the "profile." This is especially true the longer the wavelength region examined.

The intermediate wavelength region (which includes the so-called "double bond" or 6 μ region) extending roughly from 5–7 μ is a transitional region. While the bands at certain points

in the spectrum of a compound can be associated with the vibration of a structural group within the molecule, still, within limits, the position of that band (or, in other words, the particular vibration frequency of that structural group) is sensitive to changes in the molecule as a whole.

This difference in the roles that the short and long wavelength regions play in structural analysis is clear from an examination of the nature of the assignments in the two regions. While stretching vibrations of a few simple groups account for all the absorptions occurring in the 3 μ region, there are hundreds of different groups whose stretching and bending vibrations give rise to the bands in the region beyond 8 μ.

Terminology

Brief mention was made in Chapter III of the difference in attitude between the empirical and theoretical approaches to the molecular spectrum. Accurate as are the descriptions in terms of symmetry classes and general modes of vibration, they are not as useful for analytical purposes as the less accurate descriptions used in Chapter III. Since more often than not the journal references give assignments in terms of symmetry classes, it was necessary for the purpose of building up the catalogue contained in Tables 4 and 5 to translate from that type of representation to the structural analysis type with the consequent introduction of frequent questions and uncertainties in the assignments. At long wavelengths especially it becomes difficult to say what a vibration is from the structural point of view, so that finally every assignment becomes either "ring" or "chain" or "skeleton"—terms which are so general that they become useless, especially since the ranges of occurrence at the same time overlap so much and spread out so widely. A simple example of translation of terminology is methyl cyanide. In this example, the structural analysis representation fits the facts reasonably well.

Harmonics and Combination Bands

For the sake of simplicity and brevity, Tables 4 and 5 are limited to fundamental vibrations. In the case of simple molecules, it often occurs that the more complex modes of vibration are as strong as (and in some cases stronger than) fundamentals of similar frequency. As a rather striking and extreme example the main infrared bands for dimethyl acetylene, supplemented by five of the strongest Raman bands, together with assignments, are given below:

MOLECULE: METHYL CYANIDE (CH_3CN)

Theoretical Band Spectra Assignments * (Point Group C_{3v})		Structural Analysis Assignments (see Table 5 for Symbolism Key)	Frequency (cm^{-1})	Wavelength (μ)
Totally symmetric "a_1-type" vibrations	ν_1	st-s CH_3	2942	3.40
	ν_2	st C≡N	2283	4.38
	ν_3	d-s CH_3	1376	7.27
	ν_4	st CC	918	10.89
Doubly degenerate "e-type" vibrations	ν_5	st-a CH_3	3077	3.25
	ν_6	d-a CH_3	1440	6.95
	ν_7	r CH_3	1040	9.61
	ν_8	d CC≡N	380	26.3

* Herzberg, *op. cit.*, p. 332.

MOLECULE: DIMETHYL ACETYLENE ($CH_3C{\equiv}CCH_3$)

Wavelength (μ)	Frequency (cm^{-1})	Intensity	Assignment *
3.36	2975	s	fundamental (st CH_3)
4.00	2500	s	combination
4.33	2312	(Raman)	fundamental (st C≡C)
4.47	2238	(Raman)	harmonic
4.83	2065	s	harmonic and combination superposed
5.43	1841	m	combination
6.81	1468	s	fundamental (d-a CH_3)
7.25	1380	m	fundamental (d-s CH_3)
8.07	1240	m	combination
8.89	1126	w	fundamental (st-a CC)
9.52	1050	m	fundamental (r CH_3)
12.92	774	(Raman)	harmonic
14.34	697	(Raman)	fundamental (st-s CC)
17.6	568	s	combination
26.7	374	(Raman)	fundamental (d CC≡CC)

* Herzberg, *op. cit.*, p. 356.

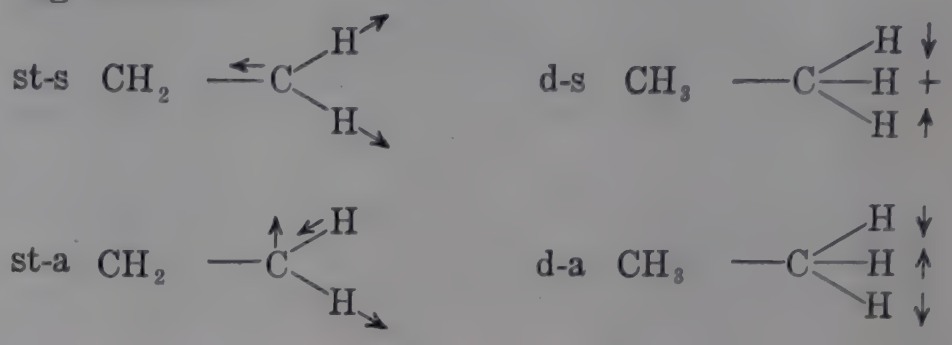
Only those marked as fundamentals appear in the wavelength catalogue (Table 5). Any attempt to identify dimethyl acetylene solely by using Table 5 would meet with failure because of the confusion introduced by the strong harmonics and combination bands being mistaken for fundamentals. The more complex molecules probably seldom have such strong combination bands. Actually, even many of the fundamentals in the spectrum of a complex compound are weak and the analyst is fortunate to have a few strong ones present with which to work. To recapitulate: While the possibility of a strong harmonic or combination band appearing in the double bond region always must be admitted, yet it is probably less likely to interfere with the use of Table 2 for the analysis of complex molecules than it would in the use of Table 5 in analysis of simple molecules.

Duplications in Spectra

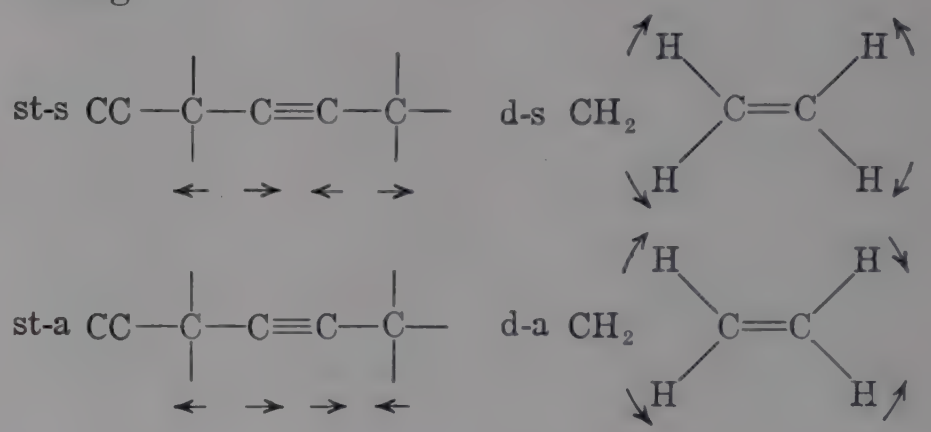
There are a number of compounds which occur in both Chapter III and Chapter IV. These are acetamide, acetone, acetoxime, acetic acid, acetyl chloride, benzene, dimethyl sulfide, ethyl mercaptan, formic acid, heavy water, hydrazine, methyl alcohol, nitromethane, pyridine, pyrrole, thiourea, urea, and water. Slight differences will be found in the wavelengths recorded in the two chapters. Aside from possible differences in purity, some if not most of the disagreements are due to the fact that the data given in Chapter III are from samples in their natural solid or liquid state, while the data compiled in this chapter are almost exclusively from gaseous samples. Care should also be taken to equate infrared data and Raman data with circumspection even for the same compound.

Note on the Meaning of "s" and "a"

While notes on the meaning of the symbolism used in the tables appear just preceding Table 5, a more extended discussion of the use of the terms "s" (symmetric) and "a" (asymmetric) is needed. As used in this chapter "s" means simply that the identical atoms in the molecular group referred to are vibrating in phase or symmetrically; "a" means that they are vibrating out of phase or asymmetrically. This is illustrated in the following sketches:



In the case of a stretching vibration in a structural group containing only two atoms, or a bending vibration in a group containing no more than three atoms, these terms "s" and "a" as used in the sketches do not apply. If, however, two identical structural groups of this simple nature occur in a single molecule, the designations "s" and "a" again are used to describe the vibration of these two groups in phase or out of phase respectively with each other as shown in the following:



This terminology cannot be carried too far because it does not specify a unique situation in more complicated molecules with more than two identical structure groups or with two identical groups containing a larger number of atoms (e.g., CH_3). It is included for the simpler cases to which it applies in order to further specify the nature of the vibration.

TABLE 3. COMPOUNDS INCLUDED IN THE WAVELENGTH CATALOGUE

Compound	*No. of Atoms*	*Journal Reference*
acetaldehyde	7	*J. Chem. Phys.* **11,** 230 (1943)
acetamide	9	*Z. physik. Chem. B.* **51,** 49 (1942)
acetic acid (monomer and dimer)	8	*J. Chem. Phys.* **6,** 534 (1938)
acetone	10	*J. Chem. Phys.* **9,** 725 (1941)
acetoxime	12	*J. Chem. Phys.* **6,** 718 (1938)
acetyl chloride	7	*Z. physik. Chem. B.* **27,** 359 (1934); **35,** 433 (1937)
acetylene	4	Herzberg, 288
allene (propadiene)	7	Herzberg, 339
ammonia	4	Herzberg, 294
ammonium bromide	6	*Z. Physik* **79,** 394 (1932)
ammonium chloride	6	*Z. Physik* **79,** 394 (1932)
ammonium nitrate	6	*Z. Physik* **79,** 394 (1932)
ammonium sulfate	6	*Z. Physik* **79,** 394 (1932)
azomethane	10	Herzberg, 357
benzene	12	Herzberg, 364
1-bromo-1-butyne	10	*J. Chem. Phys.* **12,** 156 (1944)
1,3-butadiene	10	*Z. physik. Chem. B.* **35,** 442 (1937); *J. Chem. Phys.* **11,** 432 (1943)
cis-butene-2	12	*J. Chem. Phys.* **6,** 247 (1938)
trans-butene-2	12	*J. Chem. Phys.* **6,** 247 (1938)
α-butylene	12	*Z. physik. Chem. B.* **29,** 292 (1935)
1-butyne	10	*J. Chem. Phys.* **10,** 172 (1942)
carbon disulfide	3	Herzberg, 276
carbon oxysulfide	3	*Proc. Roy. Soc. London* **140,** 605 (1933)
carbon suboxide	5	Herzberg, 303
carbon tetrachloride	5	Herzberg, 310
chlorine monoxide	3	Herzberg, 161
chloroform	5	Herzberg, 316
chloropicrin	7	*Z. physik. Chem. B.* **51,** 103 & 187 (1942)
chloro-trifluoromethane	5	*Z. physik. Chem. B.* **48,** 189 (1941)
crotonaldehyde	11	*Z. physik. Chem. B.* **27,** 176 (1934)
cyanamide	5	*Z. Physik. Chem. B.* **37,** 421 (1937)
cyanogen	4	Herzberg, 293
cyanogen chloride	3	*Z. Physik. Chem. B.* **48,** 309 (1941)
cyclobutane	12	*J. Chem. Phys.* **11,** 369 (1943)
cyclopentadiene	11	*Z. physik. Chem. B.* **33,** 179 (1936); **35,** 363 (1937); **38,** 275 (1937)
cyclopropane	9	Herzberg, 352
deutero-acetylene, C_2D_2	4	Herzberg, 289
deutero-acetylene, C_2HD	4	Herzberg, 292
deutero-acetaldehyde, CD_3CDO	7	*J. Chem. Phys.* **11,** 230 (1943)
deutero-acetic acid, CH_3COOD (monomer and dimer)	8	*J. Chem. Phys.* **6,** 534 (1938)
deutero-acetic acid, CD_3COOH (monomer and dimer)	8	*J. Chem. Phys.* **7,** 460 (1939)
deutero-acetic acid, CD_3COOD (monomer and dimer)	8	*J. Chem. Phys.* **7,** 460 (1939)
deutero-ammonia, ND_3	4	Herzberg, 294
deuterium azide	4	*J. Amer. Chem. Soc.* **61,** 2809 (1939)
1,3,5-trideutero-benzene	12	*J. Chem. Soc. London,* 1946 Part I, page 300

TABLE 3. COMPOUNDS INCLUDED IN THE WAVELENGTH CATALOGUE (*Continued*)

Compound	*No. of Atoms*	*Journal Reference*
deutero-chloroform	5	Herzberg, 316
deuterium cyanide	3	Herzberg, 280
deutero-ethylene, C_2D_4	6	Herzberg, 325
deutero-benzene, C_6D_6	12	Herzberg, 364; *J. Chem. Soc. London*, 1946 Part I, pages 252–255
deutero-ethane, C_2D_6	8	Herzberg, 344
deutero-formaldehyde, DCDO	4	Herzberg, 300
deutero-formic acid, HCOOD	5	Herzberg, 321
deutero-guanidonium	10	*Proc. Roy. Soc. London* **177,** 456 (1941)
deuterium hydrogen oxide	3	Herzberg, 282
deuterium hydrogen sulfide	3	Herzberg, 283
deutero-methyl alcohol, CH_3OD	6	Herzberg, 334
deutero-methane, CD_4	5	Herzberg, 306
deutero-methyl chloride, CD_3Cl	5	Herzberg, 314
deutero-methyl bromide, CD_3Br	5	Herzberg, 314
deutero-nitromethane	7	*J. Chem. Phys.* **11,** 361 (1943)
deuterium oxide, D_2O	3	Herzberg, 282
deutero-propionic acid, C_2H_5OOD	11	*J. Chem. Phys.* **7,** 460 (1939)
deuterium sulfide	3	Herzberg, 283
deutero-urea, ND_2COND_2	8	*Proc. Roy. Soc. London* **177,** 456 (1941)
di-acetylene	6	Herzberg, 323
ortho-dichlorobenzene	12	*J. de Phys.* **9,** 13 (1938)
meta-dichlorobenzene	12	*J. de Phys.* **9,** 13 (1938)
para-dichlorobenzene	12	*J. de Phys.* **9,** 13 (1938)
dichloro-difluoromethane (freon)	5	*J. Chem. Phys.* **7,** 553 (1939)
cis-dichloroethylene	6	Herzberg, 329
trans-dichloroethylene	6	Herzberg, 329
dicyanoethane (succinonitrile)	10	*Z. physik. Chem. B.* **29,** 274 (1935)
dimethyl acetylene	10	Herzberg, 356
dimethyl amine	10	*J. Chem. Phys.* **5,** 225 (1937)
dimethyl ammonium ion	10	*J. Chem. Phys.* **5,** 225 (1937)
dimethyl ether	9	Herzberg, 353
dimethyl sulfide	9	*J. Chem. Phys.* **8,** 60 (1940)
ethane	8	Herzberg, 344
ethyl alcohol	9	*J. Chem. Phys.* **6,** 480 (1938)
ethyl amine	10	*Z. Physik. Chem. B.* **40,** 439 (1938)
ethyl mercaptan	9	*Z. physik. Chem. B.* **40,** 439 (1938)
ethylene	6	Herzberg, 325
ethylene oxide	7	Herzberg, 341
fluorine monoxide	3	Herzberg, 161
fluoro-trichloromethane	5	*J. Chem. Phys.* **7,** 278 (1939)
formaldehyde	4	Herzberg, 300
formamide	6	*Z. physik. Chem. B.* **27,** 176 (1934); *Phil. Mag.* **19,** 1116 (1935)
formic acid	5	Herzberg, 321
furan	9	*J. Chem. Phys.* **10,** 660 (1942)
guanidonium	10	*Proc. Roy. Soc. London* **177,** 456 (1941)
hydrazine	6	*Z. physik. Chem. B.* **44,** 1 (1939)
hydrazoic acid (hydrogen azide)	4	*J. Chem. Phys.* **7,** 369 (1939)
hydrogen cyanide	3	Herzberg, 279

TABLE 3. COMPOUNDS INCLUDED IN THE WAVELENGTH CATALOGUE (*Continued*)

Compound	*No. of Atoms*	*Journal Reference*
hydrogen sulfide	3	Herzberg, 282
hydroxypropionitrile	10	*Z. physik. Chem. B.* **29,** 274 (1935); *J. Amer. Chem. Soc.* **61,** 1396 (1939)
l-iodo-1-butyne	10	*J. Chem. Phys.* **12,** 156 (1944)
methane	5	Herzberg, 306
methyl acetylene (propyne)	7	Herzberg, 337
methyl alcohol	6	Herzberg, 334
methyl amine	7	*J. Chem. Phys.* **7,** 563 (1939); *Proc. Roy. Soc. London* **173,** 339 (1939)
methyl azide	7	*J. Chem. Phys.* **8,** 369 (1940)
methyl bromide	5	Herzberg, 314
methyl chloride	5	Herzberg, 312
methyl cyanide	6	Herzberg, 332
methyl fluoride	5	Herzberg, 314
methyl iodide	5	Herzberg, 314
methyl isocyanate	7	*J. Chem. Phys.* **8,** 369 (1940)
methyl isocyanide	6	Herzberg, 332
methylene (deduced from formaldehyde)	3	Herzberg, 161
methylene chloride	5	Herzberg, 317; *J. Chem. Phys.* **12,** 310 (1944)
methylene fluoride	5	*J. Chem. Phys.* **12,** 310 (1944)
nitric acid	5	*J. Chem. Phys.* **4,** 711 (1936)
nitroethane	10	*Z. physik. Chem. B.* **51,** 187 (1942)
nitromethane	7	*J. Chem. Phys.* **8,** 314 (1940)
nitrogen peroxide (dioxide)	3	Herzberg, 284
nitrous oxide	3	Herzberg, 278
oxalyl chloride	6	*Z. physik. Chem. B.* **48,** 177 (1941); *Phil. Mag.* **23,** 1067 (1937)
phosgene (carbonyl chloride)	4	*Phil. Mag.* **25,** 98 (1939)
propane	11	Herzberg, 359
propiolic acid	7	*Z. physik. Chem. B.* **41,** 183 (1938)
propionic acid	11	*J. Chem. Phys.* **7,** 460 (1939)
propionyl chloride	10	*Z. physik. Chem. B.* **27,** 185 (1934)
propylene	9	Herzberg, 354
pyridine	11	*J. Chem. Phys.* **11,** 328 (1943); **12,** 300 (1944)
pyrrole	10	*J. Chem. Phys.* **10,** 328 (1942); **7,** 629 (1939)
sulfur dioxide	3	Herzberg, 285
tetrachloroethylene	6	Herzberg, 328
thioacetamide	9	*Z. physik. Chem. B.* **45,** 229 (1940)
thiourea	9	*Z. physik. Chem. B.* **45,** 229 (1940)
triborine triamine	12	*J. Chem. Phys.* **7,** 223 (1939)
trichloroacetamide	9	*Z. physik. Chem. B.* **51,** 187 (1942)
trichloroacetonitrile	6	*Z. physik. Chem. B.* **26,** 288 (1934)
urea	8	*Proc. Roy. Soc. London,* **177,** 456 (1941)
vinyl acetylene	8	*Z. physik. Chem. B.* **35,** 442 (1937)
water	3	Herzberg, 280

NOTE: References in "Herzberg" will be found in *Infra-red and Raman Spectra of Polyatomic Molecules,* by G. Herzberg, D. Van Nostrand Co., New York, 1945.

TABLE 4. WAVELENGTH RANGE FOR DIFFERENT VIBRATIONAL CONFIGURATIONS

Nature of Vibration		*Wavelength Range*
st	OH	2.66– 2.98
st	NH	2.94– 3.00
st	≡CH	2.95– 3.04
st	NH_2	2.88– 3.24
st	NH_3	3.03
st	NH_4	3.10– 3.28
st	CH(rg)	3.16– 3.25
st	OHO	3.19– 3.22
st	≧CH	3.16– 3.51
st	⩾CH	3.30
st	=CH_2	3.06– 3.60
st	>CH_2	3.22– 3.51
st	CH_3	3.15– 3.69
st	OD	3.59– 3.78
st	SH	3.72– 3.89
st	≡CD	3.71– 4.13
st	BH	3.97
st	ND	4.07
st	ND_2	3.84– 4.13
st	ND_3	3.91– 4.14
st	ODO	4.30– 4.37
st	CD(rg)	4.36
st	⩾CD	4.43
st	≧CD	4.47
st	=CD_2	4.26– 4.86
st	CD_3	4.30– 4.92
st	C≡N	4.31– 5.25
st	N≡N	4.67
st	=C=O	4.37– 4.88
st	C≡C	4.51– 5.68
st	=C=N	4.48
st	SD	5.00– 5.29
st-a	C=C=C	5.05– 6.37
st	C=O	5.47– 6.25
st	C=N	5.94
st	C=C	5.48– 6.60
st-a	NO_2(N=O)	6.17– 6.43
st	N=N	6.35
d	NH_2	5.95– 6.39
st	CN_2	6.77
b	OH	6.27– 7.85
d	CH_3	6.72– 7.66
st	CN_3	6.84
d	CH_2	6.63– 7.85
st	C⋯C(rg)	6.31– 7.50
d	NH_4	7.00– 7.40
st-s	NO_2(N=O)	7.25– 7.65
st-a	SO_2(S=O)	7.35
b	SH	7.76
w, r	CH	7.22–22.3
st	NN	7.78
w, r	CH_2	6.72–13.7
st	CF	8.3
st	C—(OH)	7.80– 9.71
d	ND_2	7.82– 8.38
d	ND_3	8.40
w, r	NH_2	8.90
st	COC	8.91
w, r	CH_3	6.87–13.16
st	OF	9.01
t	>CH_2	7.73–14.6
d	CD_3	8.66– 9.51
d	CC=C	8.31–11.0
d	CD_2	9.04–10.29
b	HSD	9.18
st	CCO	9.12–11.33
st	ClO	10.28
st	CN	7.19–11.89
st-s	C=C=C	9.34–11.86
st	CNC	10.75–11.19
b	SD	10.72
st	C=S	6.57–15.22
b	OD	8.49–17.0
w, r	NH	8.68–17.7
st	BN	11.75
st	OF	12.05
w, r	CD_2	11.36–14.05
w, r	CD_3	10.59–17.54
w, r	CD	10.59–21.0
st	NO	12.32
t	NH_2	13.35
b	CN	14.04
st	CCl	8.30–23.0
d	azide group	12.66–15.29
d	NO_2	15.44–16.3
st	CBr	16.47
d	CN_2	16.64
b	N=N	16.68
d	NNO	16.98
d	CF_3	17.86
d	CN_3	18.65
st	CI	18.75
b	BN	19.05
d	O=C=S	19.2
d	SO_2	19.25
d	CC≡N	19.7
b	OF	20.4
r	NO_2	16.7 –23.6
d	C=C=C	11.74–28.3

TABLE 4. WAVELENGTH RANGE FOR DIFFERENT VIBRATIONAL CONFIGURATIONS (*Continued*)

	Nature of Vibration	*Wavelength Range*
t	$=CH_2$	17.3
w, r	CH(rg)	14.9 –26.8
w, r	CD(rg)	15.1– 26.8
b	CF	22.0
d	CCO	23.0
d	CC=O	23.9
d	CCN	24.0
d	CC=C	24.0
d	COC	24.15
d	CNC	24.3
d	S=C=S	25.2
d	ClC≡N	25.3
d	CC≡N	26.3
d	CCCl	23.0 –28.7
d	CC≡C	29.8
d	CCS	30.1
t	CH_3	30.0 –42.0
b	CCl	28.0 –46.0
t	CD_3	50.0

Explanation of Table 5, the Assignment Catalogue

In the first column of the catalogue, wavelengths (in microns) are given for all absorptions whether or not they are active in the infrared. The second column lists the frequencies (in wave numbers) corresponding to the wavelengths in the first column. Intensities are indicated, whenever available, in the third column for absorption bands observed in the infrared spectrum. The intensity symbols have the following meaning:

vs = very strong
s = strong
m = medium strong
w = weak
vw = very weak
— = infrared absorption present but no indication of its intensity is given in the literature (it may be strong or weak)

Symbols in parentheses sometimes following the intensity symbol in column 3 are descriptive of the nature of the absorption band as follows:

(b) = broad absorption
(d) = partly resolved doublet (wavelength given is its average value)
(d1) = short wavelength member of a resolved doublet
(d2) = long wavelength member of the same resolved doublet
(t) = triplet absorption band (P, Q, and R branches) (zero branch wavelength value only is given)
(nr) = not resolved, i.e., this absorption band is overlapped by others

When an absorption band has not been observed in the infrared (because no infrared data are available or because vibrations producing a band at such a location are inactive in the infrared, etc.) but has been obtained from some other source (Raman spectra, etc.), symbols giving this information appear in the third column in place of the usual symbol for infrared band intensity. The meaning of these symbols is as follows:

R = Raman absorption observed only (no infrared absorption is to be expected at this wavelength since the assignment vibration is inactive in the infrared)
R_0 = Raman spectra value (there may or may not be infrared bands at this wavelength but no infrared data are available)
R_i = Raman spectra value (the vibration producing this band is active in both infrared and Raman spectra but the infrared value is uncertain due to overlapping absorptions)
C = calculated value, based on infrared and Raman data
Ci = calculated value, based on infrared data
Cr = calculated value, based on Raman data
Cx = calculated value for vibration frequency which is inactive in both infrared and Raman spectra
(sp.ht.) = calculated value for a twisting vibration based on specific heat data

In the fourth column of the wavelength catalogue are to be found the structure group assignments, i.e., the localized grouping to which the

general vibration has been reduced. Preceding the group designation is a symbol describing the mode of vibration of this group. In those cases where it was not possible to localize the vibration, use is made of the terms "ring" (rg), "chain" or "skeletal" (skel). The abbreviations employed to indicate types of vibration are as follows:

st = stretching vibration (along the bond)

b = bending vibration (across the bond): This symbol is used if the structure group vibrating is so simple that there is no more specialized description useful, or if a more specialized assignment may not be made on the basis of a limited analysis in the literature

d = deformation vibration: bending type which produces changes in the angles between atoms in the structure group itself

w = wagging vibration: bending type in which the structure group partakes of no internal changes of angle but moves as a rigid unit with respect to the rest of the molecule. The motion is a swinging back and forth in a plane perpendicular to the molecule's symmetry plane

r = rocking vibration: bending type similar to the wagging type except that the structure group swings as a unit back and forth in the symmetry plane of the molecule

t = twisting vibration: bending type similar to the wagging type except that the structure group as a whole rotates back and forth around the bond which serves to join it to the rest of the molecule

br = completely symmetric stretching vibration (breathing) usually found in ring compounds

It should be noted that in Chapter III the symbol "δ" was used to represent all sorts of "across the bond" vibrations without discrimination. The following symbols, descriptive of the vibration types, are sometimes added:

-s = symmetric (see text, page 39)

-a = asymmetric (see text, page 39)

-pp = perpendicular (usually to the plane of a ring molecule)

-pa = parallel (usually to the plane of a ring molecule)

-? = assignment is uncertain, especially the type of vibration

The fifth column is devoted to names of the compounds in which the vibrations were observed. In this column the abbreviation "(m)" implies "monomer", "(d)" implies "dimer" and "D" signifies "deutero." In the cases where it is known, the state of the compound when its spectrum was obtained is shown by the postscript letter "g" (gas), "l" (liquid) or "s" (solid).

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
2.66	3760	vs	st-a	OH	water	g
2.72	3675	m	st	OH	methyl alcohol	g
2.74	3650	s	st-s	OH	water	g
2.75	3635		st	OH	acetic acid (m)	g
2.80	3570	m	st	OH	formic acid	g
		—	st	OH	propionic acid (m)	g
2.88	3470	R	st-a	NH_2	methyl amine	g
2.89	3460	—	st	OH	D-acetic acid (m)	g
2.91	3435	—	st-a	NH_2	urea	
2.92	3425	(b)	st-a	NH_2	guanidonium	
2.93	3415	s	st-a	NH_3	ammonia	
		—	st-s	NH_2	urea	
2.94	3400	—	st	NH	pyrrole	
		w	st	NH	triborine triamine	
2.95	3390	s	st	CH	methyl acetylene	g
2.96	3380	—	st-s	NH_2	urea	
2.97	3367	R_i	st-a	OH	HDO	g
		R	st-s	CH	acetylene	g
		R_o	st	NH_2	formamide	g
		s	st-s	NH_2	methyl amine	g
		R_o	st	NH_2	thiourea	
		R_o	st	NH_2	ethyl amine	
2.98	3356	w	st-s	NH_2	hydrazine	
		—	st	OH	ethyl alcohol	g
		R_o	st	NH_2	acetamide	l
2.99	3345	s	st-s, a	CH	di-acetylene	g
		R_o	st	NH_2	formamide	g
3.00	3333	s	st-s	CH	C_2HD	g
		—	st	NH	hydrazoic acid	
		s	st-s	NH_3	ammonia	g
3.02	3311	s	st-a	CH	hydrogen cyanide	g
		R_o	st	NH_2	ethyl amine	
		s	st	CH	1-butyne	
3.03	3300	R	st	CH (acet)	vinyl acetylene	
		s	st	OH	hydroxypropionitrile	
3.04	3290	vs	st-a	CH	acetylene	g
		s	st-a	NH_2	hydrazine	
		R_o	st	NH_2	thiourea	
		—	st-s	NH_2	guanidonium	
3.05	3280	—	st	NH_2	cyanamide	
		R_o	st	NH_2	thioacetamide	
3.06	3268	R	st-a	CH_2	ethylene	g
3.07	3257	s	st-a	NH_2	hydrazine	
3.10	3225	—	st	NH_4	ammonium sulfate	
3.13	3195	R_o	st	NH_2	acetamide	g
3.14	3185	R_o	st	NH_2	thiourea	
3.15	3175	—	st	CH_3	D-acetic acid (m)	g

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	ν	I	Assignment		Name of Compound	State
3.16	3165	R	st-a	CH	cis-dichloroethylene	g
		w	st-s	NH_2	hydrazine	
		s	st	CH	furan	
3.17	3155	—	st	NH_4	ammonium nitrate	
3.18	3145	—	st	NH_4	ammonium chloride	
		—	st	NH_4	ammonium bromide	
3.19	3135	—	st-a	CH	pyrrole	
		s	st	O—H—O	propionic acid (d)	g
3.20	3125	—	st	O—H—O	acetic acid (d)	g
		—	st	CH_3	D-acetic acid (d)	g
3.22	3105	s	st-a	CH_2	ethylene	g
		vs	st	CH_2	cyclopropane	g
		R	st	CH (vinyl)	vinyl acetylene	
		—	st	O—H—O	D_3-acetic acid (d)	g
		— (d)	st-s	CH	pyrrole	
3.23	3095	s	st	CH	benzene	g
3.24	3085	s	st-a	CH	trans-dichloroethylene	g
		s	st-s	CH	cis-dichloroethylene	g
		R_o	st	NH_2	thioacetamide	
		R	st	$CH_{1,2}$	1,3-butadiene	
		—	st	CH	cyclopentadiene	
		s	st	CH	1,3,5-tri-D-benzene	g
3.25	3077	s	st-a	CH_3	methyl cyanide	g
		—	st	NH_4	ammonium nitrate	
		m	st-a	CH_2	propylene	sol'n
		s	st	CH	pyridine	g
3.26	3067	R	st-s	CH	trans-dichloroethylene	g
		—	st	NH_4	ammonium chloride	
3.27	3058	s	st-a	CH_3	methyl bromide	g
		s	st-a	CH_3	methyl iodide	g
		—	st	NH_4	ammonium bromide	
		R	st-a	CH_2	allene	l
		R	st	CH	pyridine	
3.28	3049	s	st-a	CH_2	methylene chloride	l
		—	st	NH_4	ammonium nitrate	
		s	st-a	CH_3	nitromethane	
3.29	3040	s	st-a	CH_3	methyl chloride	
3.30	3030	—	st-a	CH_2	methylene fluoride	l
		s	st	CH	chloroform	l
		vs	st	CH_2	ethylene oxide	
		—	st	CH_3	acetic acid (m)	g
		vs	st	CH_3	azo-methane	g
		m	st	$CH_{2,3}$	propionic acid (m)	g
3.31	3021	—	st-a	CH_4	methane	g
		R	st-s	CH_2	ethylene	g
		vs	st	CH_2	cyclopropane	g
3.32	3012	R_o	st-a	CH_3	acetyl chloride	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
3.32	3012	R	st	CH (vinyl)	vinyl acetylene	
		m	st	CH_2	propylene	sol'n
		vs	st	$CH_{1,2}$	1,3-butadiene	
3.33	3003	—	st-a	CH_2	(deduced from formaldehyde)	
		m	st	CH	D-formic acid	g
		R	st-a	CH_3	methyl isocyanide	
		—	st-a	CH_3	methyl azide	
		R_o	st-a	CH_3	acetamide	
3.34	2994	vs	st-a	CH_3	methyl acetylene	g
		R	st-s	CH_2	allene	
		—	st-a	CH_3	methyl isocyanate	
		R_o	st-a	CH_3	acetyl chloride	
		m	st-a	CH_3	ethane	g
		R_o	st	CH_2	hydroxyproprionitrile	
		—	st-a	CH_2	cyclobutane	
3.35	2985	s	st-s	CH_2	methylene chloride	l
		s	st-a	CH_3	methylene fluoride	l
		s	st-s	CH_2	ethylene	g
		—	st	CH_3	acetone	g
		R_o	st	$CH_{2,3}$	propionyl chloride	
		R_o	st	CH_2	dicyanoethane	
3.36	2976	s	st-a	CH_3	methyl alcohol	g
		s	st-s	CH_2	propylene	sol'n
		s	st-a	CH_3	dimethyl sulfide	
		vs (d)	st	CH_3	dimethyl acetylene	g
		R_o	st	CH_2	hydroxyproprionitrile	
		m	st-a	CH_2	propane	g
		m	st	$CH_{1,3}$	trans-butene-2	
3.37	2968	—	st-s	CH_2	(deduced from formaldehyde)	
		—	st-s	CH_2	methylene fluoride	l
		vs	st-s	CH_3	methyl-F, Cl, Br & I	
		s	st-a	CH_3	D-methyl alcohol	g
		—	st-a	CH_3	methyl amine	
		—	st-s	CH_3	nitromethane	
		s	st-a	CH_3	acetaldehyde	g
		R_o	st	$CH_{2,3}$	ethyl mercaptan	
		R_o	st	CH_3	thioacetamide	
		R_o	st	$CH_{2,3}$	ethyl amine	
		s	st-a	CH_3	propane	g
		s (b)	st	$CH_{1,2,3}$	α-butylene	
3.38	2959	m	st	CH_2	allene	g
		m	st-a	CH_3	propylene	sol'n
		m	st-a	CH_3	propane	g
		R	st	CH_2	cyclobutane	
3.39	2950	R	st-s	CH_3	methyl isocyanide	
		—	st-a	CH_3	methyl isocyanate	
		s	st-s	CH_3	ethane	g

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
3.40	2941	s	st	CH	formic acid	g
		R	st-s	CH_3	methyl cyanide	
		R	st-s	CH_3	methyl acetylene	g
		R_o	st	$CH_{2,3}$	propionyl chloride	
		R_o	st	CH_2	dicyanoethane	
3.41	2933	—	st-s	CH_3	methyl azide	
		R_o	st-s	CH_3	acetyl chloride	
		—	st	$CH_{2,3}$	ethyl alcohol	
		R_o	st	$CH_{2,3}$	ethyl mercaptan	
		R_o	st-s	CH_3	acetamide	
		R_o	st	CH_2	hydroxyproprionitrile	
3.42	2924	vs (b)	st	$CH_{2,3}$	1-butyne	
3.43	2915	R	st-s	CH_4	methane	g
		R	st-a	CH_3	acetaldehyde	
		s	st-a	CH_3	propylene	sol'n
		vs	st	CH_3	dimethyl ether	
		R_o	st	$CH_{2,3}$	ethyl amine	
3.44	2907	R_o	st	CH_3	thioacetamide	
3.45	2899	s	st-s *	CH_3	methyl amine	
		w	st-s	CH_3	dimethyl sulfide	
		—	st-s	CH_2	cyclobutane	
3.47	2882	R_o	st	CH	formamide	
		R_o	st	$CH_{2,3}$	propionyl chloride	
		m	st-s	CH_3	propane	g
3.48	2874	R_o	st	$CH_{2,3}$	ethyl mercaptan	
		s	st	$CH_{1,3}$	cis-butene-2	
3.49	2865	R_o	st	$CH_{2,3}$	ethyl amine	
3.51	2849	s	st-s	CH_3	D-methyl alcohol	g
		m	st-s	CH_3	propylene	g
3.52	2841	s	st-s	CH_3	methyl alcohol	g
3.53	2833	R_o	st	$CH_{2,3}$	ethyl amine	
3.54	2825	vs	st-a	CH_2	formaldehyde	g
3.55	2817	—	st-s *	CH_3	methyl amine	
3.59	2786	—	st-a	OD	D_2O	g
		vs	st	CH_3	acetaldehyde	
3.60	2778	s	st-s	CH_2	formaldehyde	g
3.68	2717	—	st-s	OD	HDO	g
		s	st	OD	D-methyl alcohol	g
3.69	2710	vs	st-s	CH_3	acetaldehyde	
3.71	2695	R	st-s	CD	D-acetylene	g
3.72	2688	s	st-a	SH_2	hydrogen sulfide	g
3.75	2667	R_i	st-s	OD	D_2O	g
		s	st	OD	D-formic acid	g
		—	st	OD	D-propionic acid (m)	g
3.76	2660	—	st	OD	D_3,D-acetic acid (m)	g
3.77	2653	—	st	OD	D-acetic acid (m)	g

* Alternative assignment exists.

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
3.80	2632	—	st	CD	deuterium cyanide	g
3.83	2611	R	st-s	SH_2	hydrogen sulfide	g
3.84	2604	—	st-a	ND_2	D-urea	
3.87	2584	s	st-a	CD	C_2HD	g
3.89	2571	R_o	st	SH	ethyl mercaptan	
3.91	2558	—	st-a	ND_3	D-ammonia	g
3.93	2544	— (b)	st-a	ND_2	D-guanidonium	
3.97	2519	s	st	BH	triborine triamine	
4.07	2457	—	st	ND	D-hydrazoic acid	
4.11	2433	—	st-s	ND_2	D-guanidonium	
4.13	2421	s	st-a	CD	D-acetylene	g
		—	st-s	ND_2	D-urea	
4.14	2415	—	st-s	ND_3	D-ammonia	g
4.26	2347	vs	st-a	CD_2	D-ethylene	g
4.30	2326	—	st	CD_3	D_3-acetic acid (d)	g
			st	O—D—O	D_3,D-acetic acid (d)	g
4.31	2320	R	st-s	C≡N	cyanogen	g
4.33	2309	R	st	C≡C	dimethyl acetylene	g
4.34	2304	R	st-a	CD_2	D-ethylene	g
4.35	2299	m	st	O—D—O	D-propionic acid (d)	g
4.36	2294	s	st	CD	D-benzene	g
		s	st	CD	1,3,5-tri-D-benzene	g
4.37	2288	vs	st-a	C=O	carbon suboxide	
		—	st	O—D—O	D-acetic acid (m,d)	g
		w	st-a	CD_3	D-nitromethane	g
4.38	2283	s	st	C≡N	methyl cyanide	
4.41	2268	—	st	CD_3	D_3,D-acetic acid (m)	g
4.43	2257	—	st-a	CD_4	D-methane	g
		—	st	CD	D-chloroform	l
4.44	2252	R	st-s	CD_2	D-ethylene	g
		—	st	C≡N	trichloracetonitrile	
		R_o	st	C≡N	dicyanoethane	
		R_o	st	C≡N	hydroxyproprionitrile	
4.47	2237	s	st	CD	D_3,D-acetaldehyde	
		s	st-a	CD_3	D-ethane	g
4.48	2232	—	st	C≡N	cyanamide	
		—	st	N=C=O	methyl isocyanate	
4.50	2222	vs	st-a	N≡N=O	nitrous oxide	g
4.51	2217	R_o (d)	st	C≡C	1-bromo-1-butyne	
4.54	2203	R_o	st	C≡N	cyanogen chloride	
		R	st-s	C=O	carbon suboxide	
4.55	2198	m	st-s	CD_2	D-ethylene	g
4.57	2188	R_o	st	C≡C	1-iodo-1-butyne	
4.58	2183	R	st-s	C≡C	di-acetylene	g
4.63	2160	vs	st-a	CD_2	D-formaldehyde	g
		—	st	C≡N	methyl isocyanide	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
4.63	2160	R_o	st-s	CD_3	D-nitromethane	g
4.64	2155	s	st	C≡C	methyl acetylene	
4.65	2150	s	st-a	C≡N	cyanogen	g
4.67	2141	—	st	(N_3)	hydrazoic acid	
		—	st	(N_3)	methyl azide	
4.70	2128	R	st-a	CD_3	D_3,D-acetaldehyde	
4.71	2123	R_o	st	C≡C	propiolic acid	
4.72	2118	s	st	C≡C	1-butyne (also 1-pentyne, etc.)	
4.74	2110	s	st-s	CD_3	D-ethane	g
4.75	2105	—	st	(N_3)	D-hydrazoic acid	
4.77	2096	R	st	C≡C	vinyl acetylene	
4.79	2088	R	st	C≡N	hydrogen cyanide	
		vs	st-a	CD_3	D_3,D-acetaldehyde	
4.80	2083	R	st-s	CD_4	D-methane	
4.86	2058	s	st-s	CD_2	D-formaldehyde	
4.88	2049	—	st-a	O=C=S	carbon oxysulfide	
4.92	2033	vs	st-s	CD_3	D_3,D-acetaldehyde	
4.94	2024	s	st-a	C≡C	di-acetylene	
5.00	2000	—	st-a	SD_2	deuterium sulfide	
5.05	1980	s	st-a	C=C=C	allene	
5.07	1972	R	st-s	C≡C	acetylene	
5.25	1905	R	st	C≡N	deuterium cyanide	g
5.29	1890	R	st-s	SD_2	deuterium sulfide	g
5.39	1855	Cx	st	C⋯C	benzene	
5.40	1852	m	st	C≡C	C_2HD	g
5.42	1845	Cx	st	C⋯C	D-benzene	
5.47	1828	—	st	C=O	phosgene	g
5.48	1825	s	st-a	C=C	1,3-butadiene	g
5.56	1793	R_o	st	C=O	acetyl chloride	
5.60	1786	R_o	st	C=O	propionyl chloride	
5.63	1776	R_o	st	C=O	oxalyl chloride	
5.65	1770	—	st	C=O	acetic acid (m)	g
		—	st	C=O	D-acetic acid (m)	g
		s	st	C=O	propionic acid (m)	g
5.67	1764	vs	st	C=O	D-formic acid	g
5.68	1761	R	st-s	C≡C	D-acetylene	g
		s	st	C=O	D_3-acetic acid (m)	g
		s	st	C=O	D_3,D-acetic acid (m)	g
5.70	1754	s	st	C=O	propionic acid (d)	g
		s	st	C=O	D-propionic acid (m)	g
5.73	1745	—	st	C=O	(esters in general)	
5.74	1742	vs	st	C=O	formaldehyde	g
5.75	1739	vs	st	C=O	formic acid	g
		vs	st	C=O	acetaldehyde	
		—	st	C=O	acetic acid (d)	g
		—	st	C=O	D_3,D-acetic acid (d)	g
5.76	1736	—	st	C=O	D-acetic acid (d)	g

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
5.78	1730	vs	st	C=O	D_3,D-acetaldehyde	
		s	st	C=O	D_3-acetic acid (d)	g
5.80	1724	vs	st	C=O	acetone	g
		s	st	C=O	D-propionic acid (d)	g
		w	st	C=C ring	pyridine	
5.83	1715	R_o	st *	C=O	propiolic acid	
5.88	1700	vs	st	C=O	D-formaldehyde	
5.93	1686	—	st	C=O	crotonaldehyde	
5.94	1683	—	st	C=N	acetoxime	
5.95	1681	R	st d	C=O NH_2	urea	
5.98	1672	R_o	st	C=O	formamide	
5.99	1669	—	d	NH_2	guanidonium	
6.02	1661	R_o	st	C=O	acetamide	
6.06	1650	R_o	st *	C=O	propiolic acid	
6.07	1647	s	st	C=C	propylene	
		s	st	C=C	butene-1 and butene-2	
6.11	1637	—	st	C=C	α-butylene	
6.15	1626	vs	b-a	NH_3	ammonia	g
		m	d	NH_2	methyl amine	
6.16	1623	R	st	C=C	ethylene	g
6.17	1621	vs	st-a	NO_2	nitrogen peroxide	g
6.20	1613	—	st	C=O	D-urea	
		—	d	NH_2	trichloroacetamide	
6.21	1610	R_o	d	NH_2	acetamide	
		m	st	B=N	triborine triamine	
6.23	1605	R_o	st-a	NO_2	chloropicrin	
		R	d	NH_2	urea	
6.25	1600	R_o	st	C=O	formamide	
		s	st	C=C	vinyl acetylene	
		s	st	C=C ring	pyridine	
6.26	1597	s (d)	st-s	C=C	1,3-butadiene	
6.27	1595	vs	b	OH	water	g
6.29	1590	s	st	C=C	cis-dichloroethylene	
6.31	1585	s	d-a	NH_2	hydrazine	
		R	st	C=C	benzene	
6.32	1582	s	st-a	NO_2	nitromethane	
6.33	1580	—	b	NH_2	cyanamide	
		s	st-a	C=C ring	furan	
6.34	1577	R	st	C=C	trans-dichloroethylene	
6.35	1575	R	st	N=N	azo-methane	
		w (b)	st	C=C	1,3,5-tri-D-benzene	g
6.37	1570	vs	st-a	=C=(CO)	carbon suboxide	
		R	st	C=C	tetrachloroethylene	g
		s	st-a	NO_2	D-nitromethane	g
6.39	1565	—	d	NH_2	guanidonium	

* Alternative assignment exists.

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
6.42	1558	R	st	C=C	D-benzene	g
6.43	1555	R_o	st-a	NO_2	nitroethane	
6.54	1529	s	st-a	ring	pyrrole	
6.55	1527	C	d	CH_4	methane	g
6.57	1522	s	st-a	C=S	carbon disulfide	
6.58	1520	Cx	w	CH	benzene	
6.60	1515	R	st	C=C	D-ethylene	g
6.63	1508	—	d	CH_2	methylene fluoride	l
6.65	1504	s	d	CH_2	formaldehyde	
		R	d-a	CH_2	cyclopropane	g
6.69	1495	m	d-s	CH_2	ethylene oxide	
6.71	1490	vs	st-s	ring	furan	
6.72	1488	—	w	CH_2	methylene fluoride	l
		w	d-a	CH_3	nitromethane	
		w	d	CH_2	1,3-butadiene	g
6.73	1486	s	d-a	CH_3	ethane	g
		s (t)	st	C=C	benzene	
6.75	1481	—	d	CH_3	methyl azide	
		s	st	C=C ring	pyridine	
6.76	1479	s	d	CH_3	D-methyl alcohol	g
		Cx	w	CD	D-benzene	g
6.77	1477	m	d	CH_3	methyl alcohol	g
		R	st-a *	CN_2	urea	
6.78	1475	s	d-s	CH_3	methyl fluoride	
6.79	1473	m	d-a	CH_3	propylene	g
6.80	1471	m	d-a	CH_3	methyl fluoride	
6.81	1469	vs (t)	d & d-a	$CH_{2,3}$	propane	g
		s	d-a	CH_3	dimethyl acetylene	g
6.82	1466	vs	d-s, a	CH_3	dimethyl ether	g
		s	st-s	ring	pyrrole	
		s	st	B=N	triborine triamine	
6.84	1462	—	st-a	CN_3	guanidonium	
6.85	1460	s	d	CH_3	D-methyl alcohol	
		s	d	CH_3	methyl amine	
		s	b	$CH_{2,3}$	1-butyne	
6.86	1458	m	d-a	CH_3	methyl chloride	
		R_o	d	$CH_{2,3}$	nitroethane	
6.87	1456	R	d-a	CH_3	methyl isocyanide	
		m	d	CH_3	methyl alcohol	
		—	w, r & d-a	$CH_{2,3}$	ethyl alcohol	
6.88	1453	w	d-a	CH_2	ethylene oxide	
		—	d	CH_3	methyl isocyanate	
		— (d)	d-s, a	CH_2	cyclobutane	
6.90	1449	w	d-a	CH_3	nitromethane	
		—	b	$CH_{2,3}$	α-butylene	
6.91	1447	s	d-a	CH_3	propylene	

* Alternative assignment exists.

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	ν	I	Assignment		Name of Compound	State
6.92	1445	—	b	CH_2	(deduced from formaldehyde)	
		m	d-a	CH_3	methyl bromide	
		vs	d-a	CH_3	acetaldehyde	
		vs	d-a	CH_3	dimethyl sulfide	
		s	st	C═C ring	pyridine	
6.93	1443	s	d-a	CH_2	ethylene	g
6.94	1441	m	d-a	CH_3	methyl iodide	
		—	d-a	CH_3	methyl cyanide	
6.95	1439	vs	d	CH_3	methyl acetylene	g
6.96	1437	R_o	d	$CH_{2,3}$	nitroethane	
6.97	1435	—	d	CH_3	methyl azide	
6.98	1433	R	d-s	CH_2	allene	g
		s (d)	d-a	CH_2	cyclopropane	g
		w	d	CH_2	1,3-butadiene	g
6.99	1431	vs (d)	d	CH_3	azo-methane	
		vs	d	CH_3	acetone	g
7.00	1429	s	d	CH_2	methylene chloride	
		—	b	NH_4	ammonium nitrate	
7.02	1425	—	d	CH_3	methyl amine	
7.05	1418	—	b	NH_4	ammonium sulfate	
		R_o	d	CH_3	acetyl chloride	
		—	d	CH_3	acetic acid (d)	g
		s	st-a	ring	pyrrole	
7.06	1416	w	d	CH_2	propylene	
		—	b	$CH_{2,3}$	α-butylene	
7.07	1414	R	d-s	CH_3	methyl isocyanide	
		vs	d-a	CH_3	acetaldehyde	
7.08	1412	—	b	NH_4	ammonium chloride	
		—	st d-s	N═C═O CH_3	methyl isocyanate	
7.09	1410	—	b	NH_4	ammonium bromide	
		w	d	CH_2	vinyl acetylene	
		R_c	d	CH_3	acetamide	
7.10	1408	s	st	C⋯C	1,3,5-tri-D-benzene	g
7.13	1403	R_o	b	CH_2	propionyl chloride	
7.14	1401	—	b	D—O—H	HDO	g
7.15	1399	w	d-s	CH_3	propylene	
7.17	1395	R_o	b	$CH_{2,3}$	nitroethane	
7.19	1391	R_o	st	skel	acetamide	
7.20	1389	s	d-a	CH_2	allene	g
7.21	1387	—	d	CH_3	D-acetic acid (d)	g
		m	st-s	ring	furan	
7.23	1383	m (d)	b	CH	1,3-butadiene	
		s	st-s	NO_2	nitromethane	g
		s	st-s	NO_2	D-nitromethane	g
		m	st-s	ring	pyrrole	
7.24	1381	—	d	CH_3	acetic acid (m)	g

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	ν	I	Assignment		Name of Compound	State
7.25	1379	R_o	r	CH_2	ethylene oxide	
		s	d-s	CH_3	ethane	g
		m	d-s	CH_3	dimethyl acetylene	
7.26	1377	—	d	CH_3	methyl isocyanate	
		—	d	CH_3	D-acetic acid (m)	g
7.27	1376	R	d-s	CH_3	methyl cyanide	
7.28	1374	s (d)	d-s	CH_3	ethane	g
7.30	1370	vs	d-s	CH_3	acetaldehyde	
7.32	1366	R_o	st-s	NO_2	nitroethane	
7.35	1361	—	st-a	SO_2	sulfur dioxide	g
7.36	1359	R_o	d	CH_3	acetyl chloride	
7.38	1355	s	d-s	CH_3	methyl chloride	
7.40	1351	—	b	NH_4	ammonium nitrate	
		—	d	CH_3	methyl azide	
7.41	1349	R_o	d	CH_3	acetamide	
7.45	1342	R	d-s	CH_2	ethylene	g
7.46	1340	m	b	OH	methyl alcohol	g
7.50	1333	m	st	C═C	D-benzene	g
7.56	1323	vs	d-s	CH_3	dimethyl sulfide	
7.57	1321	s (d)	b	$CH_{2,3}$	1-butyne	
7.58	1319	w	st-s	NO_2	nitrogen peroxide	
7.62	1312	w	r	CH_3	methylamine	
7.65	1307	R_o	st-s	NO_2	chloropicrin	
7.66	1305	—	d	CH_4	methane	g
		s	d-s	CH_3	methyl bromide	
7.67	1304	s	r	CH	cis-dichloroethylene	
7.72	1295	—	st	(N_3)	methyl azide	
7.73	1294	—	t	CH_2	methylene fluoride	
		—	b	$CH_{2,3}$	α-butylene	
7.74	1292	R_o	st	N═O	nitric acid	
7.76	1289	vs	b	SH	hydrogen sulfide	
		—	b	CH	vinyl acetylene	
7.77	1287	—	b	CH	propylene	g
7.78	1285	vs	st-s	N≡N═O	nitrous oxide	
7.80	1282	m	d-s	NH_2	hydrazine	
		—	st	CO	acetic acid (d)	g
7.81	1280	s	r	CH_2	formaldehyde	
7.82	1279	—	d	ND_2	D-guanidonium	
		R	t	CH_2	propane	g
7.85	1274	—	b d-s	OH CH_2	ethyl alcohol	g
7.86	1273	m	b	CH	1,3-butadiene	g
7.87	1271	R	r	CH	trans-dichloroethylene	
7.88	1269	—	st	(N_3)	hydrazoic acid	
7.90	1266	vs	w	CH_2	methylene chloride	l
		—	st	CO	acetic acid (m)	g

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
7.90	1266	—	st	CO	D-acetic acid (m)	g
7.91	1264	w	r	CH	furan	
		R_o	b	$CH_{2,3}$	nitroethane	
7.92	1263	—	r	CH_2	methylene fluoride	l
		s	st-a	CO	ethylene oxide	
7.94	1259	w	r	CH_3	dimethyl sulfide	
		—	w	CH_2	cyclobutane	
7.95	1258	—	st	CO	D-acetic acid (d)	g
7.96	1256	—	b	$CH_{2,3}$	α-butylene	
7.99	1252	s	d-s	CH_3	methyl iodide	
8.00	1250	vs (b)	r	$CH_{2,3}$	1-butyne	
8.08	1238	R	r	CH	pyrrole	
8.14	1229	—	w	CH_2	cyclobutane	
8.17	1224	m (nr)	r	CH_2	propylene	g
8.27	1209	—	t	CH_2	cyclobutane	
8.30	1205	vs	b	CH	chloroform	l
		—	st-a	CF, CCl	chloro-trifluoromethane	
8.31	1203	R	b	C═C—C	1,3-butadiene	
8.32	1202	s	d	CH_3	acetone	g
		w	r	CH	pyridine	
8.33	1200	—	r	CH	trans-dichloroethylene	g
		—	r	CH_2	cyclobutane	g
8.36	1196	m	r	CH_3	methyl fluoride	g
8.38	1193	—	r	CH_3	methyl azide	
		—	d	ND_2	D-guanidonium	
8.40	1190	—	b-a	ND_3	D-ammonia	g
		Cx	r	CH	benzene	g
8.41	1189	R	st		cyclopropane	g
		s	st-s	ring	furan	
8.47	1181	—	r	CH_3	methyl isocyanate	
		s	w & r	CH_3	dimethyl ether	g
8.48	1179	R	r	CH_3	D-methyl alcohol	g
		R	r	CH	cis-dichloroethylene	g
		m	r	CH_2	propane	g
8.49	1178	s	b	OD	D_2O	g
		R	r	CH	benzene	g
8.50	1176	—	st	CC	acetic acid (m & d)	g
8.54	1171	R	r	CH_3	methyl alcohol	
8.55	1170	R	r	CH_3	ethane	g
8.57	1167	s	w	CH_2	formaldehyde	g
8.58	1166	w (nr)	r	CH_2	propylene	g
8.59	1164	—	d	ND_2	D-urea	
8.62	1160	Cx	r	CH	benzene	g
8.64	1157	R	st-a *	CN_2	urea	
8.66	1155	w	t	CH_2	methylene chloride	l

* Alternative assignment exists.

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

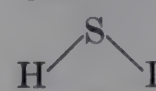
λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
8.66	1155	s	d-a	CD_3	D_3,D-acetaldehyde	
8.67	1153	w	r	CH_3	nitromethane	
8.68	1152	—	b	NH	hydrazoic acid	
		m	r	$CH_{2,3}$	propane	g
8.69	1151	—	st-s	SO_2	sulfur dioxide	g
		s	w & r	CH_2	ethylene oxide	
8.70	1149	—	t	CH_2	methylene chloride	l
8.72	1147	—	st-a	CF	freon	
8.73	1145	Cx	w	CH	benzene	g
8.74	1144	s	r st (br)	NH C—C ring	pyrrole	
8.80	1136	w	r	CH	pyridine	
8.85	1130	m	d-a	CD_3	D_3,D-acetaldehyde	
		R	b	$CH_{2,3}$	nitroethane	
8.87	1127	s (dl)	w	CH	acetaldehyde	
8.88	1126	s	r	NH_2	methyl amine	
8.89	1125	w	st-a	CC	dimethyl acetylene	g
8.91	1122	m	st-a	C_2O	dimethyl ether	g
8.92	1121	R_o	r	NH_2	trichloroacetamide	
8.93	1120	—	st	N=C=N	cyanamide	
		R	w	CH_2	ethylene oxide	
		R_o	b	NH_2	acetamide	
8.94	1119	—	r	CH_3	methyl azide	
9.01	1110	—	st-a	F_2O	fluorine monoxide	
		s	st-a	CN	azo-methane	
		—	t	CH_2	cyclobutane	
9.02	1109	s (d2)	w	CH	acetaldehyde	
9.03	1107	—	r	CH_3	methyl isocyanate	
9.04	1106	s	d	CD_2	D-formaldehyde	
9.07	1103	s	d	CD_3	D-ethane	
9.09	1100	R_o	b	$CH_{2,3}$	nitroethane	
		m	r	CH	1,3,5-tri-D-benzene	
9.10	1099	m	b	NH	triborine triamine	
9.12	1096	m	r	CH_3	nitromethane	
		—	st-a	C—C—O	ethyl alcohol	
9.15	1093	vs	st	CO	formic acid	
9.17	1091	—	st-a	CF & CCl	chloro-trifluoromethane	
		—	b	C=C—C	vinyl acetylene	
9.18	1089	—	b		HDS	
9.24	1082	—	st-a	CF & FCCl	freon	
		w	r	NH	hydrazine	
		R_o	st-a	C_2N	dimethylamine	
9.25	1081	m (b)	r	$CH_{2,3}$	1-butyne	
9.26	1080	—	b	CH	1,3-chlorobenzene	
9.28	1078	s	d-a	CD_2	D-ethylene	g
9.29	1076	R_o	st	CC	oxalyl chloride	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
9.29	1076	vs	r	CH	pyrrole	
9.32	1073	s	r	CH	furan	
9.34	1071	R	st-s	C═C	allene	g
		s	d	CD_3	D-ethane	g
9.35	1070	w	st-a	CF & CCl	fluoro-trichloromethane	
		R	st-s	C—C—C	acetone	
		Cx	w	CD	D-benzene	g
9.42	1062	R	w	CH	pyridine	
9.45	1058	—	b	C═C—C	vinyl acetylene	
		—	t	CH_2	cyclobutane	g
9.47	1056	R	r	CH_3	methyl alcohol	
9.49	1054	C	d	CD_4	D-methane	g
9.50	1053	m	r	CH_3	propane	g
9.51	1052	—	w & r	$CH_{2,3}$	ethyl alcohol	
		m	d	CD_3	D-nitromethane	g
9.52	1050	Cr	r	CH_2	ethylene	g
		m	r	CH_3	dimethyl acetylene	g
9.54	1048	vs	st	CF	fluoro-methane (methyl fluoride)	
9.55	1047	R_o	st	CC	ethyl amine	
9.56	1046	—	st	CN	methyl amine	
		vs	r & w	CH	pyrrole	
9.59	1043	vw (nr)	r	CH_3	propylene	g
9.61	1041	—	r	CH_3	methyl cyanide	
		R	r	CH_3	methyl isocyanide	
		vs	st	CO	D-methyl alcohol	
		w	r	CH_3	methyl acetylene	
9.64	1037	vs (dl)	r	CH_3	dimethyl sulfide	
		s	b-pp	C—C—C ring	pyridine	
		s (t)	r	CH	benzene	g
9.67	1034	vs	st	CO	methyl alcohol	g
9.70	1031	m	r	CH_2	allene	g
9.71	1030	s	st	CO	D-formic acid	
9.72	1029	R_o	st-a	C_2N	dimethyl ammonium ion	
9.73	1028	s	w	CH_2	cyclopropane	g
		R	b-pa	C—C—C ring	pyridine	
9.77	1024	vs (d2)	r	CH_3	dimethyl sulfide	
9.78	1022	R	t-s	CH_2	ethylene oxide	
9.80	1020	—	b	CH	1,2-dichlorobenzene	
9.85	1015	m	r	CH_3	methyl chloride	
		—	st-s	CN	guanidonium	
		vs	r	CH	pyrrole	
9.86	1014	s	d	C═C—C	1,3-butadiene	g
9.87	1013	s	r	CH_3	azo-methane	
9.90	1010	—	b-s	ring	1,4-dichlorobenzene	
		—	st	ring	cyclobutane	
9.92	1008	—	st-s	CN_2	urea	
9.94	1006	R_o	st	skel	nitroethane	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
10.00	1000	R	st-a	CCl	tetrachloroethylene	
		R_o	b	NH_2	acetamide	
10.01	999	vs	r	CH	furan	
10.03	997	—	st-s	CN_2	D-urea	
10.04	996	—	d	CD_4	D-methane	g
		w (nr)	r	CH_3	propylene	g
10.05	995	m	r	CH_2	ethylene	g
10.07	993	R	st	CC	ethane	g
10.08	992	R	st	CC	benzene	g
10.10	990	s	r	CD_2	D-formaldehyde	
		R	st	CC ring	pyridine	
		—	st	ring	cyclobutane	
		—	b–s	ring	1,3-dichlorobenzene	
10.19	981	R	d-s	CD_2	D-ethylene	g
10.28	973	—	st-a	Cl_2O	chlorine monoxide	
10.33	968	s	b-s	NH_3	ammonia	g
		R_o	st	CC	ethyl mercaptan	
10.36	965	s	r	NH_2	hydrazine	
10.44	958	—	b	C═C—C	vinyl acetylene	
10.47	955	R_o	st	CC	acetyl chloride	
10.49	953	—	st	CC	D-acetic acid (m, d)	g
10.50	952	m	r	CH_3	methyl bromide	
10.54	949	vs	w	CH_2	ethylene	g
10.59	944	s	w	CD	D_3,D-acetaldehyde	
		R	st	C═C	D-benzene	g
		w	r	CD_3	D-nitromethane	g
10.60	943	R	w	CH_2	ethylene	
10.61	942	s (dl)	st	CC	methyl acetylene	g
10.62	941	R	r	CH_3	D-methyl alcohol	
10.64	940	s	st-s	C_2O	dimethyl ether	
		m	w	CH	pyridine	
		—	st	ring	cyclobutane	
10.66	938	s	w	CD	D-formaldehyde	
10.68	936	vw	b	CH	propylene	g
10.70	935	—	b	C═C—C	vinyl acetylene	
10.72	933	—	b	SD	deuterium sulfide	g
10.74	931	s (b)	b-s	NH	ammonia	g
10.75	930	s	b	NH	hydrazine	
		R_o	st-s	C_2N	dimethyl amine	
		—	st	CC	acetoxime	
		Cx	r	CD	D-benzene	g
10.78	928	R	st	CN	methyl isocyanide	
10.80	926	s (b)	w	CH & CD	1,3,5-tri-D-benzene	
10.83	923	—	r	CH_2	cyclobutane	
10.85	922	R	st-s	CN	azo-methane	
		m	st-a	CC	propane	g
10.86	921	s (d2)	st	CC	methyl acetylene	g

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

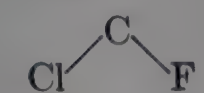
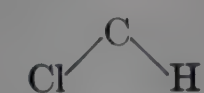
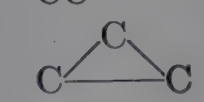
λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
10.86	921	m	st	CN	nitromethane	
		—	st	CN	D-guanidonium	
10.88	919	—	st-a		freon	
		s	st	CC	propylene	g
10.89	918	—	st	CC	methyl cyanide	
10.90	917	s (b)	st	CC	acetaldehyde	
10.91	917	s	r		trans-dichloroethylene	
		m	b?	NH	triborine triamine	
10.94	914	—	st	CN	methyl azide	
10.95	913	vs	st-a	CCl	tetrachloroethylene	
10.96	912	—	st	CN	cyanamide	
11.00	909	vs	b st?	C=C—C CC	1,3-butadiene	g
11.01	908	—	b	CD	D-chloroform	l
11.09	902	—	r	CH_2	cyclobutane	
11.11	900	—	st	CC	α-butylene	
11.14	897	m (d)	r	CH_2	methylene chloride	
11.16	896	—	r	CH_3	acetone	g
11.17	895	R_o	st-s	C_2N	dimethyl ammonium ion	
11.20	893	R_o	st	CN	ethyl amine	
11.24	890	s	r	CH_3	acetaldehyde	
11.31	884	w	b-pp	C—C—C	pyridine	
11.33	883	Cr	r	CD_2	D-ethylene	g
		—	st-s	C—C—O	ethyl alcohol	g
11.36	880	m	r	CH_3	methyl iodide	
11.38	878	s	st	CN	D-nitromethane	g
11.40	877	—	st-a	CCl	freon	
11.43	875	R	st	CC	vinyl acetylene	
11.47	872	—	st	NC	methyl isocyanate	
		vs	r	CH_2	cyclopropane	g
		s	b-a	ring	furan	
11.49	870	w	st-s	CC	propane	g
11.52	868	vs	d		cyclopropane	
		m	w	CH	pyrrole	
11.53	867	R	r	CD	D-benzene	g
11.55	866	vs	st-s	CO	ethylene oxide	
11.59	863	s	b	OD	D-methyl alcohol	
11.63	860	m	st	CC	D_3,D-acetaldehyde	
		R_o	b	skel	acetamide	
		—	b	CH	1,3-dichlorobenzene	
11.64	859	—	st-s	C=S	carbon oxysulfide	
11.67	857	s	st-a	CCl	cis-dichloroethylene	
11.74	852	vs	b	C=C=C	allene	g
		R	st	CC	D-ethane	g

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

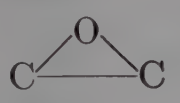
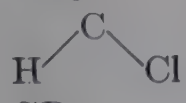
λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
11.75	851	R	st	BN	triborine triamine	
11.76	850	—	st	NN	hydrazine	
		—	st	CC	α-butylene	
		—	b	CH	1,2-dichlorobenzene	
11.78	849	R	w	CH	benzene	g
11.79	848	R	st	NC—CN	cyanogen	
11.83	845	—	st-a	CCl	phosgene	
11.85	844	R	t-s	CCl	trans-dichloroethylene	
11.86	843	R	st-s	=C=CO	carbon suboxide	
		R_o	st	skel	nitroethane	
11.89	841	R_o	st	CN	chloropicrin	
11.93	838	—	b	ring	pyrrole	
12.00	833	w	st-a	CF & CCl	fluoro-trichloromethane	
		s (b)	r	CD	1,3,5-tri-D-benzene	
12.05	830	—	st-s	FO	fluorine monoxide	
		—	b	CH	1,4-dichlorobenzene	
12.12	825	C	t	CH_2	ethylene	
12.20	820	s	st	CCl	trans-dichloroethylene	
		(sp. ht.)	t	CH_2	allene	g
		s	r	CH_3	ethane	g
		—	st	CCl	1,2- & 1,3-dichlorobenzene	
12.25	816	Cx	r	CD	D-benzene	g
12.27	815	—	b	NH	hydrazine	g
12.29	814	—	w & r	$CH_{2,3}$	ethyl alcohol	g
12.30	813	s (t)	r	CD	D-benzene	g
12.32	812	—	st	NO	acetoxime	
12.38	808	w	b		ethylene oxide	
12.55	797	—	st-a	CCl_4	carbon tetrachloride	l
12.66	790	—	b	(N_3)	methyl azide	
12.77	783	—	st-s	CF & CCl	chloro-trifluoromethane	
12.79	782	vs	st-s	CCl_2	tetrachloroethylene	
12.82	780	R	w	CD_2	D-ethylene	g
12.92	774	s	d	NH_2	methyl amine	
		m	st-a	C—C—C	acetone	g
12.99	769	—	t	ring	1,3-dichlorobenzene	
13.02	768	—	st-a	CCl	carbon tetrachloride	l
		s	b	NH & CH	pyrrole	
13.11	763	s	w	CH	furan	
13.16	760	m	st-a	CCl	chloroform	l
		m	r	CH_3	acetaldehyde	
13.19	758	R	b		trans-dichloroethylene	
13.25	755	m	r	CD_3	D_3,D-acetaldehyde	
13.33	750	—	t	ring	1,2-dichlorobenzene	
13.35	749	—	b-a	ND	D-ammonia	g
		R	t	NH_2	hydrazine	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

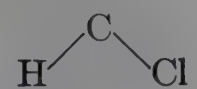
λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
13.37	748	s	r	CH_3	propane	g
13.39	747	w	w	CH	pyridine	
13.51	740	R	t	CH_2	cyclopropane	g
		—	r	CH	1,3-dichlorobenzene	
13.54	739	—	b	(N_3)	hydrazoic acid	
13.56	738	—	st-a	CCl	D-chloroform	l
13.57	737	vs	st-a	CCl	methylene chloride	l
13.66	732	vs	st	CCl	chloroform	l
13.70	730	—	st	CCl	cyanogen chloride	
		—	r	CH	1,4-dichlorobenzene	
13.72	729	vs	b	≡CH	acetylene	g
13.79	725	s	b-s	ring	furan	
13.89	720	vs	w	CD_2	D-ethylene	g
13.95	717	s	?	ring?	triborine triamine	
14.04	712	R_o	b	CN	chloropicrin	
14.05	712	vs	b	CH	hydrogen cyanide	g
		Ci	r	CD_2	D-ethylene	g
14.06	711	R	st-a	CCl	cis-dichloroethylene	
		R	w b-s	CH ring	pyrrole	
14.08	710	m	w	CH	pyridine	
14.16	706	—	st	C_2S	dimethyl sulfide	
14.20	704	vs	st-s	CCl	methylene chloride	l
14.34	697	R	st-s	CC	dimethyl acetylene	g
14.41	694	s	r		cis-dichloroethylene	
14.47	691	s (t)	w	CH	1,3,5-tri-D-benzene	
14.60	685	w	t-a	CH_2	ethylene oxide	
		—	st-s	C_2S	dimethyl sulfide	
14.64	683	s	b	CH & CD	C_2DH	
14.71	680	—	st-s	ClO	chlorine monoxide	
		—	br	ring	1,4-dichlorobenzene	
14.75	678	—	b	CH (acet)	vinyl acetylene	
14.90	671	s (t)	w	CH	benzene	g
14.92	670	—	br	ring	1,3-dichlorobenzene	
14.95	669	s	w	CH	pyridine	
14.99	667	w	st-s	CCl	chloroform	
15.06	664	—	st-s	CF & CCl	freon	
15.12	661	R	w	CD	D-benzene	
15.20	658	—	b	(N_3)	hydrazoic acid	
15.22	657	—	st	CS	ethyl mercaptan	
15.24	656	R	st-s	C═S	carbon disulfide	g
15.29	754	—	b	(N_3)	methyl azide	
15.34	652	—	b	N═C═O	methyl isocyanate	
		m	b-s	C—C—C ring	pyridine	
15.36	651	—	st-s	CCl	D-chloroform	l
15.38	650	—	br	ring	1,2-dichlorobenzene	
15.43	648	s	d	NO_2	nitrogen peroxide	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

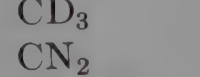
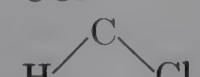
λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
15.46	647	s	d	NO_2	nitromethane	
		R	b-a	ring	pyrrole	
15.53	644	R	st	CC	di-acetylene	g
15.58	642	vs	b	C≡C—H	methyl acetylene	g
		R_o	b	C≡C—H	1-butyne	
15.60	641	—	st	CCl	1,4-dichlorobenzene	
15.80	633	R_o	b	C≡C—H	1-pentyne (also 1-hexyne)	
15.82	632	m	d	NO_2	D-nitromethane	g
15.90	629	—	r	NH	methyl amine	
15.95	627	—	d	ring	cyclobutane	
16.03	624	s	b-a	ring	furan	
16.07	622	m	b	BH	triborine triamine	
16.13	620	m	b		trans-dichloroethylene	
16.21	617	—	b	chain	vinyl acetylene	
16.30	613	R_o	d	NO_2	nitroethane	
16.35	612	R	b	C≡C—H	acetylene	
16.37	611	vs	st	CBr	methyl bromide	
16.47	607	—	b	N=C=O	methyl isocyanate	
16.51	606	R	b-pa	CC	benzene	g
16.64	601	s	r	CD_3	D-ethane	g
		R	d	CN_2	urea	
16.66	600	m	b-pp	CC ring	pyridine	
16.68	600	R	b	C—N=N—C	azo-methane	
16.70	599	m	r	NO_2	nitromethane	
16.80	595	—	b-pa	ring	cyclobutane	
16.90	592	w	d	ring	1,3,5-tri-D-benzene	
16.95	590	—	st	CCl	acetyl chloride	
16.98	589	s	b	N—N—O	nitrous oxide	g
17.04	587	—	b	CD	D-hydrogen cyanide	g
17.06	586	R	b	C=O	carbon suboxide	
17.24	580	C	t	CD_2	D-ethylene	g
17.30	578	s	t	$C=CH_2$	propylene	g
17.34	577	R	b-pa	CC	D-benzene	g
17.36	576	—	st-s	CCl	phosgene	
17.54	570	s	b		cis-dichloroethylene	
		m	r	CD_3	D_3,D-acetaldehyde	
17.7	565	—	b	NH	pyrrole	
17.8	562	R_o	b	skel	acetamide	
17.86	560	—	d	CF	chloro-trifluoromethane	
		w	r	NO_2	D-nitromethane	g
18.3	546	—	b	C—C—C	acetone	
18.5	541	—	d	ring	1,2- & 1,3-dichlorobenzene	
18.55	539	vs	b	≡CD	D-acetylene	
18.65	536	—	b	CN_3	guanidonium	
18.7	535	s	st-s	CF, CCl	fluoro-trichloromethane	
		—	b	chain	vinyl acetylene	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

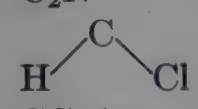
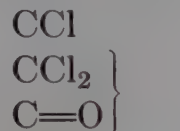
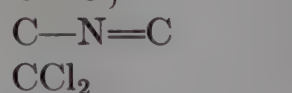
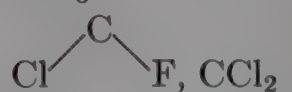
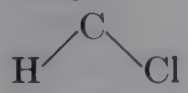
λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
18.75	533	s (t)	w	CD	1,3,5-tri-D-benzene	
		vs	st	CI	methyl iodide	
19.05	525	m	b	BN	triborine triamine	
19.2	521	—	b	O=C=S	carbon oxysulfide	
19.25	520	—	b	C=C—C=C	1,3-butadiene	
		—	b	SO_2	sulfur dioxide	
19.30	518	s	b	CC	C_2HD	
19.4	515	s	r	CH	acetaldehyde	
19.6	510	C	b	ring	pyrrole	
19.75	506	R	b	C≡N	cyanogen	
19.8	505	Ci	b	C≡C	D-acetylene	g
20.15	497	s (t)	w	CD	D-benzene	
20.4	490	—	b	F_2O	fluorine monoxide	
20.6	485	R_o	st	CCl	trichloroacetonitrile	
20.8	481	—	b	CF, CCl	chloro-trifluoromethane	
20.9	478	m	r	CD	D_3,D-acetaldehyde	
21.0	476	m	r	NO_2	nitromethane	
21.75	460	R	st-s	CCl	carbon tetrachloride	l
22.0	455	—	d	CF, CCl	freon	
22.3	448	R	b	CH	di-acetylene	g
22.4	446	R	st-s	CCl	tetrachloroethylene	
22.5	444	R	w	C=O	phosgene	
22.7	441	R_o	r	NO_2	chloropicrin	
22.9	436	—	b	CC	α-butylene	
23.0	435	R_o	b	C—C—Cl	acetyl chloride	
		R_o	st?	CCl	propionyl chloride	
23.1	433	—	d	CF, CCl	freon	
		—	d	C—C—O	ethyl alcohol	
23.2	431	R_o	b	skel	acetamide	
23.5	426	—	b	C—C=O	acetaldehyde	
23.6	424	w	r	NO_2	D-nitromethane	g
23.9	418	—	b	C—C=O	D_3,D-acetaldehyde	
24.0	417	—	b	C=C—C	propylene	g
		—	b	C—C—N	ethyl amine	
24.1	415	R_o	d	C_2N	dimethyl amine	
		m	?	ring	triborine triamine	
24.15	414	R	d	C_2O	dimethyl ether	
24.3	412	R_o	d	C_2N	dimethyl ammonium ion	
24.6	407	R	t		cis-dichloroethylene	
24.7	405	R	b-pp	CC ring	pyridine	
24.75	404	R	b-pp	CC ring	benzene	
25.2	397	—	d	CF, CCl	fluoro-trichloromethane	
25.25	396	s	b	S=C=S	carbon disulfide	
25.3	395	—	b	Cl—C≡N	cyanogen chloride	
25.9	386	—	d-a	CCl_2	tetrachloroethylene	
26.3	380	—	b	C—C≡N	methyl cyanide	
26.7	375	R	b	CC chain	dimethyl acetylene	

TABLE 5. A STRUCTURAL ASSIGNMENT CATALOGUE FOR THEORETICALLY ANALYZED MOLECULES (*Continued*)

λ	$\bar{\nu}$	I	Assignment		Name of Compound	State
26.7	375	R	b	CC chain	propane	g
		R	b-pp	CC ring	pyridine	
26.8	373	R	w	CH, CD	1,3,5-tri-D-benzene	
27.3	367	—	d-s	CCl_3	D-chloroform	
27.5	364	—	d-s	CCl_3	chloroform	l
28.2	355	—	d	CF, CCl	chloro-trifluoromethane	
28.3	353	R	b	C═C═C	allene	
		—	b	CN	methyl isocyanate	
28.6	350	m	d	CF, CCl	fluoro-trichloromethane	
		R	r	CCl	trans-dichloroethylene	
28.7	348	—	b	C—C—Cl	acetyl chloride	
29.8	336	R	b	C≡C—C	methyl acetylene	
29.9	334	—	b		acetoxime	
30.0	333	C	t *	CH_3	propane	g
30.1	332	—	w or r	CCl_2	tetrachloroethylene	
		R_o	b	C—C—S	ethyl mercaptan	
30.3	330	—	b	ClO	chlorine monoxide	
31.25	320	—	t		freon	
32.8	305	—	d	CCl	carbon tetrachloride	
33.3	300	R	b r	CCl_2 C═O	phosgene	
34.5	290	R	b	C—N═C	methyl isocyanide	
35.3	283	R	d	CCl_2	methylene chloride	l
36.4	275	C	t	CH_3	ethane	g
37.0	270	s	t (int. rot.)	OH	methyl alcohol	
38.2	262	—	d-a	CCl_3	D-chloroform	
38.5	260	—	t		freon	
		—	d-a	CCl_3	chloroform	l
38.6	259	—	b	CN	methyl azide	
40.1	249	m	d	CF, CCl	fluoro-trichloromethane	
42.2	237	R	d-s	CCl_2	tetrachloroethylene	
42.9	233	C	t	CH_3	methyl amine	
43.3	231	R	b	CC	di-acetylene	
44.25	226	s	b	NC—CN	cyanogen	
45.9	218	R	d	CCl	carbon tetrachloride	l
46.9	213	—	b	chain	dimethyl acetylene	g
50.0	200	C	t	CD_3	D-ethane	g
		C	t *	CH_3	propane	g
57.8	173	R	b		cis-dichloroethylene	
61.3	163	R_o	st	C—CN	trichloracetonitrile	
68.9	143	—	b-pp	ring	cyclobutane	

* Alternative assignment exists.

Chapter V

APPLICATION OF THE INFRARED METHOD IN PRACTICE

The two general types of problems in the identification of organic molecules were mentioned in Chapter II as being (1) the rationalization of one of a series of proposed structures with the actual absorption spectrum, and (2) the proposal of possible elementary groups present in an unknown structure by analysis of the absorption spectrum and from general chemical and physical evidence. Eventually, the second problem always drifts into the first one during the progress of a complete investigation. The examples which are described in this chapter should in no sense be regarded as complete investigations.

The first problem is handled by the previously described techniques of band interpretation and requires little discussion, but a number of examples will be cited. The usual method is to take the structures proposed and note the bands which would be expected for each on a basis of the general knowledge. This work may often require new model compounds. The structure which most nearly fits the spectrum is then subjected to chemical verification and further comparison with models of closer identity.

Among the amide spectrograms is one, ϵ-phenyl caproamide (Plate 78), submitted for testing when the compounds of this group were being collected.[10] The chemist was reasonably certain that this was the correct structure from the analysis and method of preparation, although the latter was a little unusual. Examination of the spectrum shows that the identification is certainly correct, for all five bands which are to be expected from this group were present.[11]

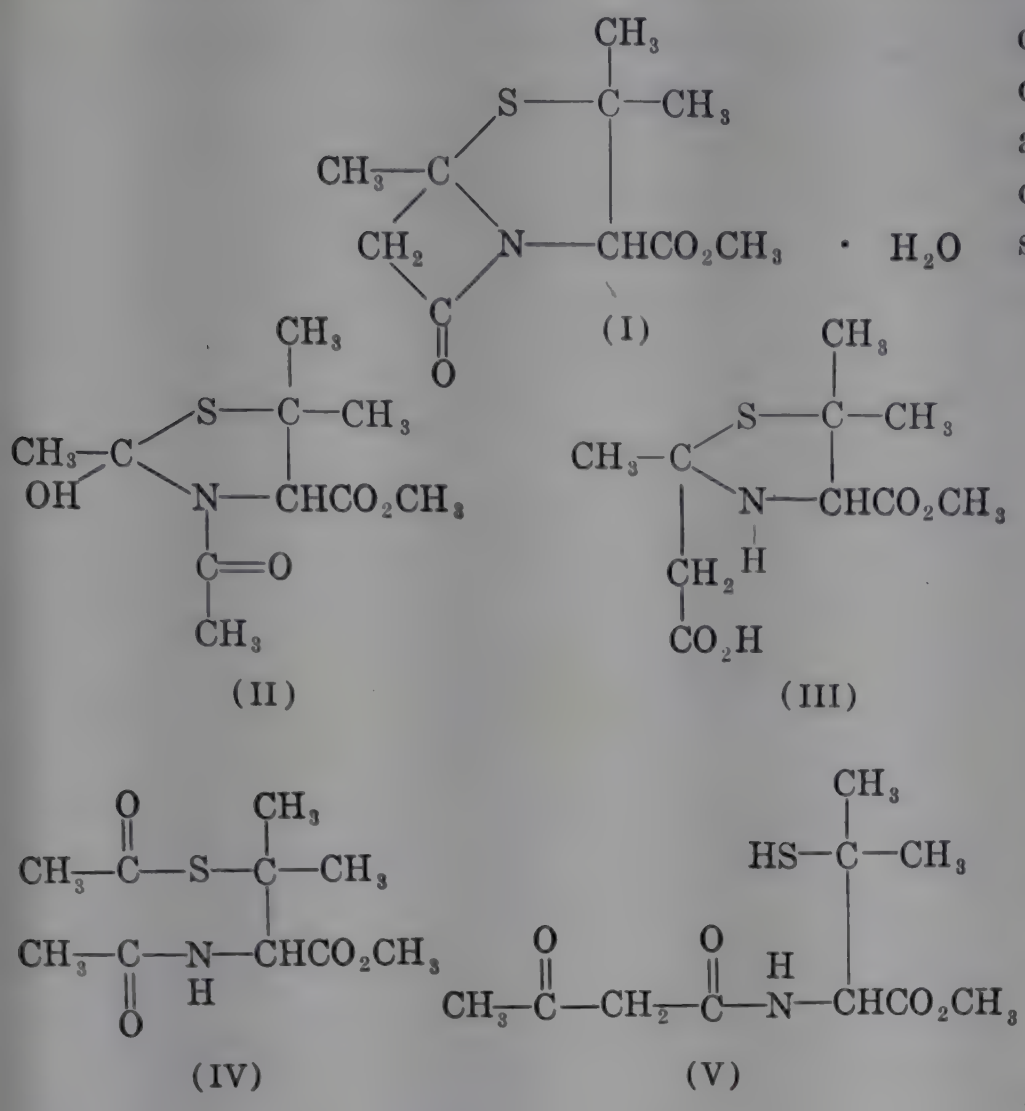
Frequently, the information that the spectrum is incompatible with a given structure can be sufficiently positive to make such evidence of value. Thus, the compound listed in some current catalogues as 2-mercapto-thiazoline should have absorptions at 4.0 μ for the SH group and between 5.9 μ and 6.3 μ for the C=N group. Instead, it has a band at 3.20 μ and another at 6.61 μ. These were interpreted as an NH group band and the complex sulfur-nitrogen absorption described on p. 5. The new proposed structure was therefore 2-thio thiazolidone.

(I) (II)

Attempts to prepare compound I in the University of Michigan chemistry laboratory always led to compound II, making it somewhat doubtful if compound I can exist without rearrangement. Subsequent chemical tests for SH were also negative.

As a second example of this approach, a white crystalline compound of analysis $C_{10}H_{17}NO_4S$ was obtained from the reaction of 2,5,5-trimethyl-Δ^2-thiazoline-4-carboxylic methyl ester and ketene.[12] The chemical analysis indicated the addition of one molecule of ketene and one of water, the source of the water being unknown. A number of formulae were proposed for the resulting compound, among which were:

[10] L. Wick, University of Michigan.
[11] Cf. Chapter II, p. 10.
[12] Courtesy of W. E. Bachmann and E. Jenner, University of Michigan.



(I)

(II)

(III)

(IV)

(V)

The spectrum is given in Plate 1. Significant bands occur at 3.04 μ, 5.74 μ, 5.90 μ, 6.06 μ and 6.47 μ. Formulas of the type of I, II and III can be eliminated for lack of enough double bonds or appropriate special groups to account for the absorptions. Either IV or V would be satisfactory, for the amide group would account for the bands

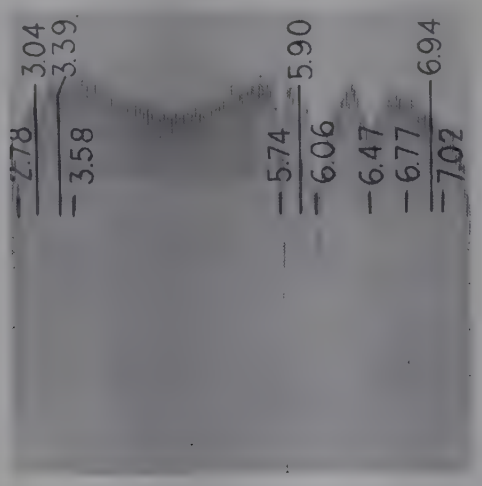


PLATE 1. NS-Acetyl-β,β-dimethylcysteine.

at 3.04 μ, 6.06 μ and 6.47 μ, the known ester corresponds to the 5.74 μ band, and the 5.90 μ band could be caused by either the thiolester carbonyl of IV or the ketone carbonyl of V. Compound IV was then synthesized and found to be identical with the unknown. From these results the chemists concluded that the original thiazoline had contained considerable uncyclized N-acetyl-β,β-dimethylcysteine. The acid corresponding to compound V was later identified tentatively in another series of experiments, and the spectrum of it is given in Plate 2 for a comparison of the similarities.

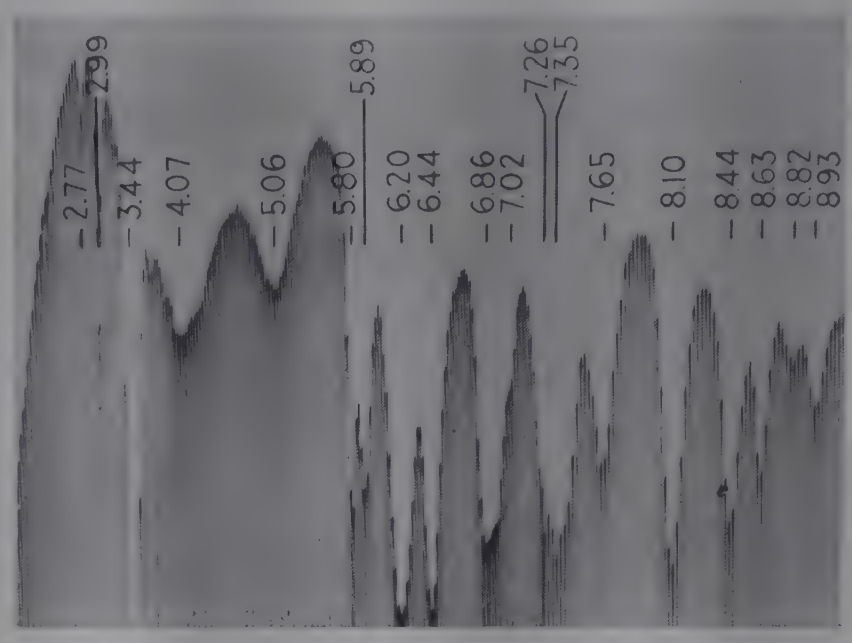


PLATE 2. N-Acetoacetyl-β,β-dimethylcysteine.

The more difficult phase of the general problem is the second one, namely, proposing possible structural elements in an unknown compound. Here it is easier to give negative than positive information, although even the negative information is often subject to reservations. When the compound is completely unknown, the history of the process is often helpful. In treating N-benzoyl-N-methyl urethane with phosphorous trichloride a mobile oil was obtained which was definitely not the expected acid chloride.[13] The spectrum is given in Plate 3. Significant bands occur at 3.0 μ, 3.25 μ, 6.00 μ, 6.24 μ, 6.31 μ, 6.5 μ and 6.70 μ. It will be noted that there is no band in the vicinity of 5.6 μ, definitely ruling out the acid chloride carbonyl structure. The bands at 3.25 μ, 6.24 μ, 6.31 μ and 6.70 μ are characteristic of a conjugated phenyl group. Considering the origin of the compound, the strong band at 6.0 μ is probably from an N-benzoyl group. The bands at 3.0 μ and 6.5 μ are properly located to be accounted for by N-methyl benzamide, but they are rather too weak, and this compound is clearly not N-methyl benzamide from its other physical properties. On the whole, the spectrum most nearly resembled that of N,N-dimethylbenzamide. The chemists therefore made the suggestion that this was N-chloro-N-methylbenzamide, which

[13] Courtesy of W. E. Bachmann and Marshall Cronyn, University of Michigan.

would probably carry some N-methylbenzamide in solution from hydrolysis, and so could account for the weak 3.0 μ and 6.5 μ bands. No further attempt was made to confirm this, but the identification seemed positive.

The previously mentioned ketene-thiazoline reaction is a very interesting one from the chemical standpoint. Very little is known about ketene

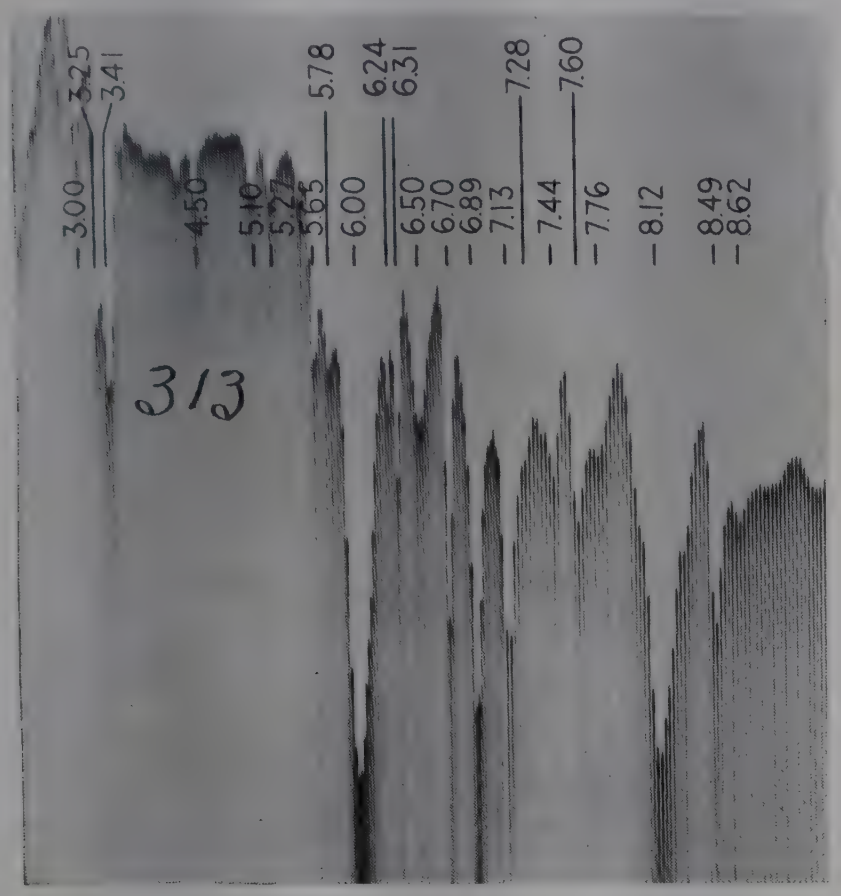


PLATE 3. N-chloro-N-methyl benzamide.

as a reagent at present, and in application to thiazolines a number of totally unknown compounds were produced.[14] Partial infrared studies were made of four of these compounds. The chemical evidence with some help from infrared analysis established structures for three of these, but, in the case of the fourth, the structure which has been tentatively accepted is not fully correlated with the infrared spectrum. These compounds are treated here not so much as examples of successful infrared interpretations but as an illustration of the beginnings and approaches which are the basis of the method. Time did not permit of more than single spectrum interpretations.

The fourth compound was actually the parent compound of the series, and resulted from the addition of two molecules of ketene to one mole-

[14] W. E. Bachmann, E. Jenner and W. J. Scott, University of Michigan.

cule of 2,5,5-trimethyl-thiazoline-Δ^2-4-carboxylic acid methyl ester. The spectrum is given in Plate 4. There are bands at 5.74 μ, 5.94 μ, 6.05 μ and 6.54 μ. There are no bands at 3 μ other than those of the CH vibrations. Therefore there is neither NH nor OH present. There is no SH, nor would it have been expected. The only known band combination which would couple two or

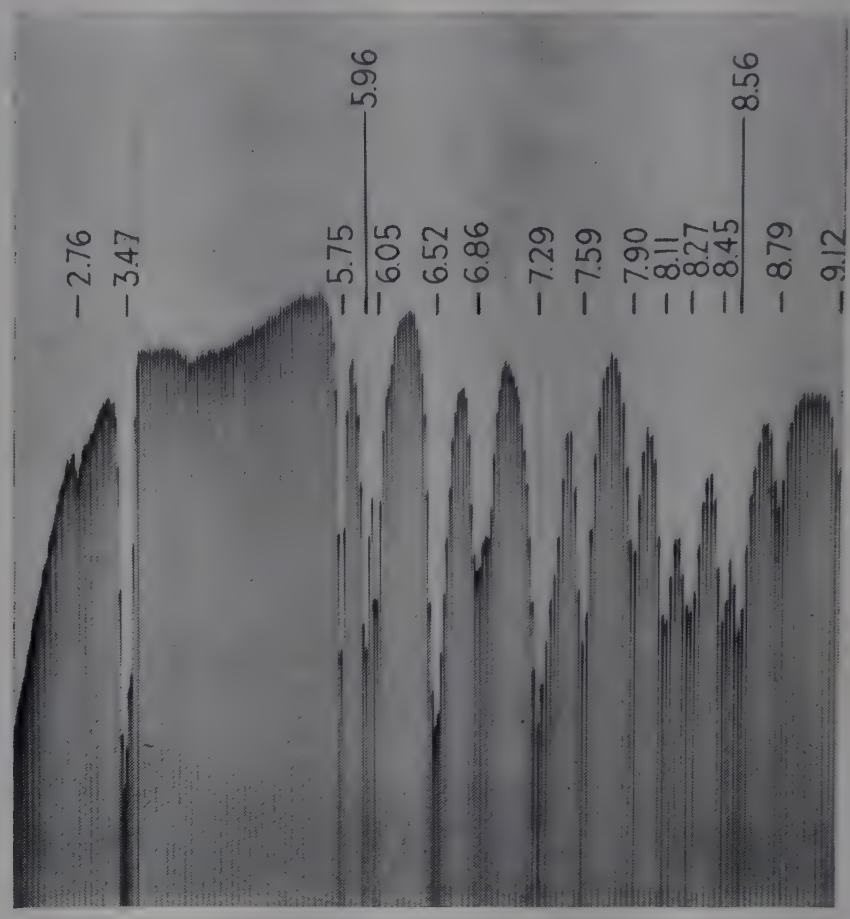


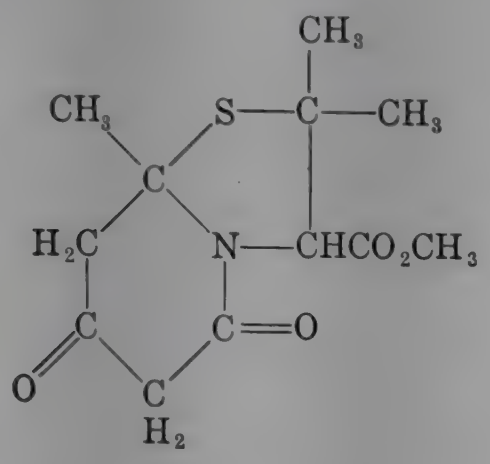
PLATE 4. Ketene reaction product from 2,3,3 trimethyl thiazoline-4-carboxylic acid methyl ester.

more bands in this case is the amide group, but the NH band at 3.0 μ is absent, so this is not a possibility. The four bands must apparently be interpreted separately. An ester group was known to be present in the original molecule. This type of reaction would not be expected to affect it. Therefore, the band at 5.74 μ may be securely assigned to this group. From its occurrence at the normal 5.75 μ position, it is also unlikely that it has become conjugated in any way. The band at 5.94 μ is in an indeterminate region, but its intensity indicates that it cannot be from a C=C vibration. From their similarity in shape and intensity to the 5.74 μ band it might be surmised that the 5.94 μ and 6.05 μ bands have their origin in carbonyl vibrations. The 5.94 μ band could be caused with about equal likelihood by a thiolester, lactam, or ketone carbonyl. There is also a very slight possibility that it is caused by a conjugated

ester group, or even a straight chain C=N. By a similar consideration of the known structure groups, the 6.05 μ band is most likely to have its origin in an N-acyl carbonyl group, but might arise from almost any type of C=N group or even a conjugated ketone.

The band at 6.54 μ is anomalous, since none of the known sources of bands in this region seems admissible in this case. Neither the amide, carboxylate ion, thioureide ion, or nitro group is chemically possible here.

The structure assigned to this compound by the chemists, on a basis of the degradation reactions, was that which was expected from the reaction, namely,

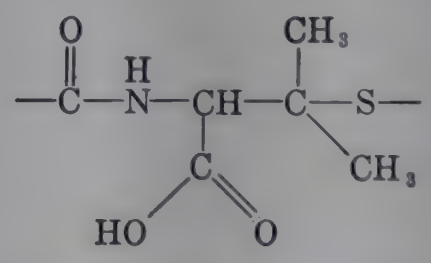


Except that there does not seem to be any adequate explanation of the 6.54 μ band, the spectrum is quite compatible with the structure suggested. The 5.94 μ band is easily assigned to the ketone carbonyl of the piperidione ring, and the 6.05 μ band can arise from the N-acyl carbonyl in the same ring. There is no NH or OH as required. Assigning an origin to the 6.54 μ band has been of considerable interest, but has met with no success thus far. From the knowledge that this region is occasionally invaded by absorptions from the single-bonded vibrations of nitrogen, this atom in the molecule seems most likely to be involved. Model compounds of this type, however, do not in general have such an absorption. Currently, therefore, the knowledge of this compound must be regarded as unsatisfactory, owing largely to the cursory nature of the infrared studies made upon it.

The second compound which will be considered was obtained by treating the previous compound briefly with methanol and alkali and then acidifying it. About 5 mg of a definite compound were produced but it was found to be difficult to repeat the preparation. The entire sample was dedicated to an infrared test, with the result that this is the only information available on the material. Fortunately, the infrared results were fairly conclusive. Reference to the spectrum in Plate 2 will show that there are absorptions at 2.99 μ, 4.07 μ, 5.06 μ, 5.80 μ, 5.89 μ, 6.20 μ and 6.44 μ. The band at 2.99 μ is from either NH, OH or both (the resolution on a salt prism is not always enough to separate close bands here at 3.0 μ). Bands like the ones at 4.07 μ and 5.06 μ have been observed repeatedly in the spectra of the α-amido acids, although not all such acids show them and their origin is not at all understood.[15] Turning to the double-bond region with these facts in mind, it is next desirable to consider what combinations can be made of these bands. A pairing of the bands at 6.20 μ and 6.44 μ, as arising from an amide group, —CO—NH—, is greatly strengthened by the presence of the necessary NH group band at 2.99 μ and is further supported by the two amido acid group bands at 4 μ and 5 μ. It is then easy to recognize the band at 5.80 μ as being in the appropriate place for bands of the acid carbonyl of an amido acid.

This leaves only one band (at 5.89 μ) requiring assignment. Reference to the information on bands at this wavelength, either in the table in Chapter IV, or in the classifications of Chapter I, shows that of the types of carbonyl vibrations described there this band might be caused by either another acid group, a ketone, lactam, or thiolester.

This is as much as can be said from the spectrum alone, but from a knowledge of the chemistry of the compound it is possible to go further. If the compound is an α-amido acid, it certainly involves the structure



since this is basic to the parent compound. It is now required to place another carbonyl bond somewhere. The lactam is clearly impossible since the only nitrogen atom is already in use. To complete the structure as a thiolester would give

[15] Cf. p. 13 and records of this type of compound.

NS-diacetyl-β,β-dimethylcysteine, a compound which was previously examined (p. 67) and which does not have the same spectrum.

It is difficult to rule out a second acid group, especially in view of the lack of knowledge of the empirical formula, but the chemists did not feel that any reaction which would give such a compound could be even likely here. Comparison of the spectrum with that of N-acetyl-β,β-dimethylcysteine showed a strong similarity, especially in the structure of the region between 3.5 μ and 4.1 μ, for the ester and $C_9H_{13}O_3NS$ for the acid. Plates 5a and 5b give these spectra. The ester compound shows significant bands at 3.10 μ, 5.72 μ, 6.23 μ and 6.50 μ. The acid compound has corresponding bands at 3.03 μ, 5.87 μ, 6.39 μ and 6.60 μ, with two more bands at 4.19 μ and 5.25 μ. The bands at 5.72 μ and 5.87 μ obviously arise from the ester and acid carbonyl groups, respectively, and so may be dismissed from further consideration.

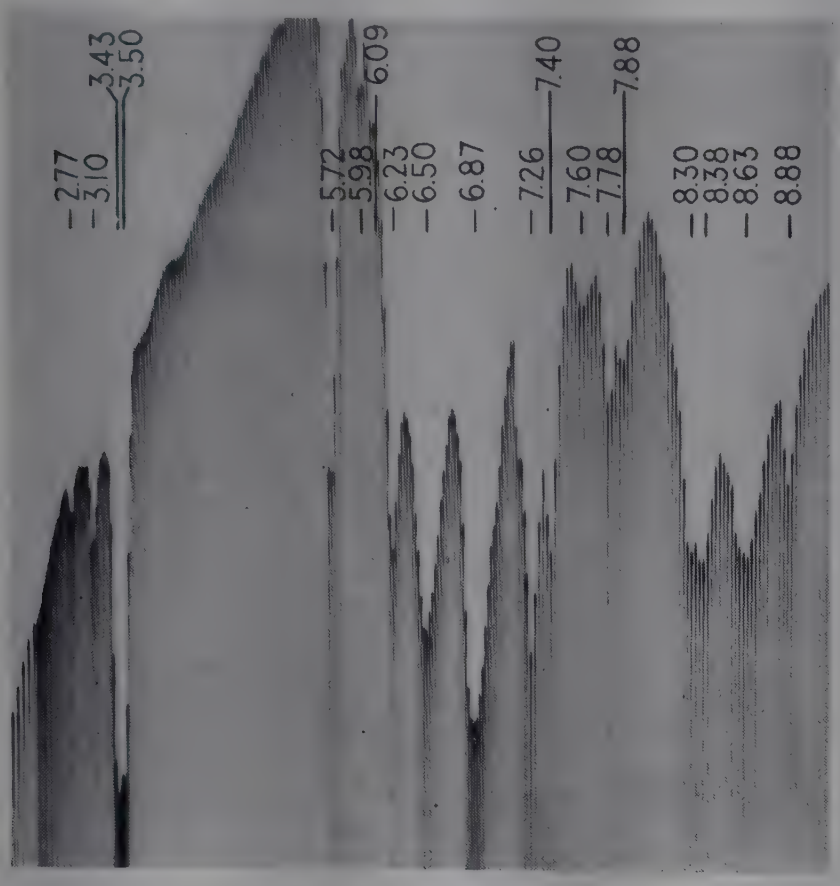


PLATE 5a. Methanolysis product.

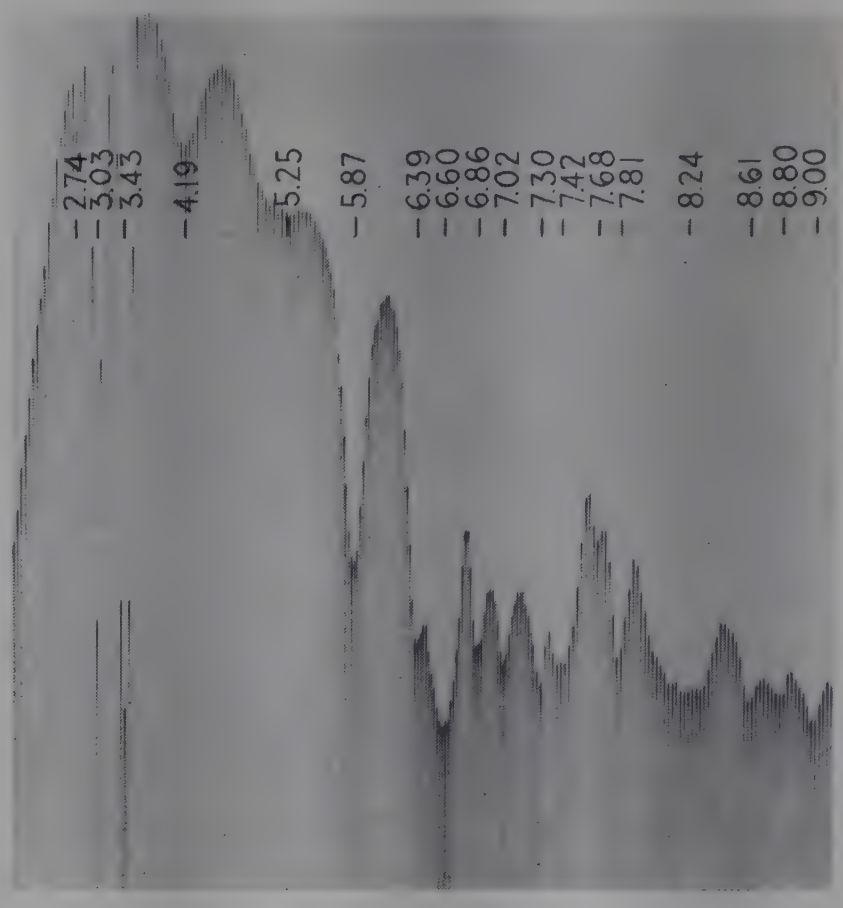


PLATE 5b. Alkali hydrolysis product.

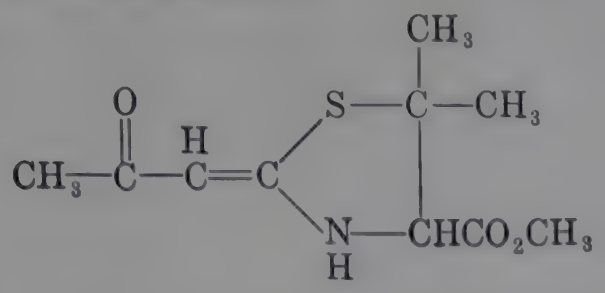
where the band of the SH vibration is expected to occur but is masked by the amido acid group bands. Thus, the ketone was advanced as the most likely group to account for the 5.89 μ band, and the final structure proposed, N-aceto-acetyl-β,β-dimethylcysteine, met with general favor both as explaining the infrared spectrum and as a likely transitory product in the sequence of reactions being studied. It might be remarked that admission of N-acetoacetyl-β,β-dimethylcysteine as a degradation product would greatly strengthen the chemical evidence for the piperidione structure of the parent product.

The third and fourth compounds were an ester and acid having the same basic structure. These compounds were obtained by further treatments of the parent compound, the ester in particular coming from methanolic HCl degradation. The empirical formulae were established as $C_{10}H_{15}O_3NS$

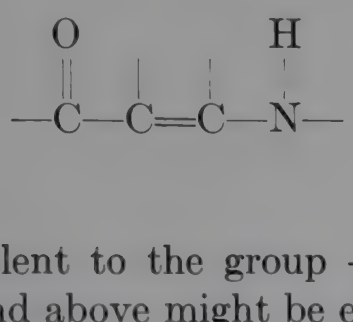
As in the previous instance, the combination which springs to mind immediately on seeing the entire set of bands observed in the acid is an α-amido acid group. The 4.19 μ and 5.25 μ bands make this especially appealing, but the extreme position and low intensity of what would need to be called the Amide I band at 6.39 μ are certainly deterrents. It seems probable now from the chemical behavior of this compound that the α-amido acid is an unacceptable structure. When this became evident, the chief pertinent and certain fact from the infrared data was that OH or NH was present, as shown by the 3.10 μ band in the spectrum of the ester.

As with the other compounds of the series, the burden of the effort lay on the shoulders of the chemists, since this problem was not specifically one in which the University of Michigan OSRD infrared group was concerned. From extended

degradation experiments, they concluded that it must have the structure



One of the most interesting aspects of these compounds is the pair of bands at 4 μ and 5 μ, which have heretofore been found only with amido acids. At present it is not known how these bands arise. When this is understood it may be found that the conditions are fulfilled here. Organic chemists cite a generalization which they call "the principle of vinylology," in which it is asserted that the effects of any given group are transmitted through the vinyl group. If this principle may be extended into the interpretation of the infrared spectrum, the group



may be equivalent to the group , and so the compound above might be expected to give a spectrum somewhat similar to that of an amido acid. This point will bear further investigation.

It is necessary to emphasize at this point that the foregoing examples have dealt only with what information could be obtained from the simple 3–8 μ absorption spectrum of a compound in combination with other standard chemical or physical data. In fairness to the infrared method it must be recognized that, when the desire for knowledge about a particular compound justifies giving special attention to it (as was not the case with any of these which have been mentioned as examples), then there are many other means of securing evidence which may be brought to bear. Deuterization, for example, can be used to bring out the location of the labile hydrogen atoms, and thus the presence of an amide group in compounds III and IV could quite rigorously have been tested as discussed in Chapter II. An excellent example of the application of a variety of methods to the structure of one compound will be found in the infrared section of the forthcoming monograph of the National Academy of Sciences on penicillin chemistry, where the infrared approach to the structure of penicillin will be discussed.[16]

To many the procedure in identifying molecular structure groups will now be self-evident if it was not so already. Many others will prefer to pioneer new lines of approach in their mental organization of the problem. At the risk, therefore, of becoming didactic a summary of the methods implied in the foregoing examples has been included as a series of steps which can be made to glean the evidence available from the mere absorption spectrum alone. These are:

1. Record all bands of intensity greater than 10% between 2.8 μ and 3.4 μ; 3.5 μ and 5.4 μ; and 5.4 μ and 6.8 μ. Give these strong bands primary consideration. Weak bands may later be considered in searches for SH, phenyl rings, or C=C bonds which might be suspected of producing conjugation effects with some of the stronger bonds.
2. Bands in the first region mentioned in (1) may be securely assigned to NH, OH or both. Absence of a band is usually excellent negative evidence.
3. Bands in the second region should be scrutinized for their possible assignment to carboxylic acids, hydrochlorides, sulfhydryl, triple bond, α-amido, or amino acid absorptions. Research is needed to clarify this region.
4. Bands in the third or double-bond region must be considered in combinations which might be attributable to a single group. The known combinations have been described at length in Chapter II.
5. The extent to which the absorptions in the 3–5 μ regions confirm or supplement these combinations must be considered.
6. The likelihood of conjugation and symmetry combinations among the structural groups responsible for the strong bands should be weighed.
7. If all or certain bands must be given independent significance, the structure groups that are possible explanations of them, without considering conjugation, should be enumerated. Such typical structure groups

[16] Under OSRD agreement, the authors are not permitted to enlarge on this subject here.

may be found either by the use of Chapter I, or the table of Chapter III.

8. Since C=C bonds can be of extremely low intensity and still exercise a full effect on the location of a band which may be of far greater intensity, it is necessary to consider the possibility that a lone band has been shifted by .1 μ to .2 μ to longer wavelengths from its normal position. Usually it is desirable to locate some indication of the C=C group absorption which might be coupled with this.
9. Consider the possibility of bands of multiple significance (such as those assigned to urethane carbonyls).
10. Look in the long wavelength region for supporting evidence for NH_2 amides, esters, ethers, phenyl groups, nitro groups.
11. If records are available not taken in a paraffin base, the types of CH bending vibrations present may be noted. Methyl, methylene and isopropyl groups are easily distinguished.

When the problem degenerates into that under (7), the chemical and physical evidence available from other sources becomes of immense importance helping as it does to eliminate trivial bands and irrelevant structures from consideration; and to confirm the interpreter's conjectures.

Practice Spectra

The only way that one can acquire the skills and experience which these techniques require is by examining the spectra of a great variety of compounds, and by making actual interpretations himself. To facilitate the former, the spectra of some three hundred and twenty-five diversified compounds have been reproduced in full. To accomplish the latter, 11 compounds have been selected and their spectra are given in Plates 6 to 16. It is suggested that the reader who needs experience in analysis may find it interesting and worthwhile to derive, first of all, as much information as possible from these spectra alone, and then to take the physical and chemical data on each compound which might with reason be known and carry the identification on further if possible. Finally, the structural formulas for these compounds should be scrutinized so that experience may be gained in the use of hindsight as a supplement to foresight.

The interpretations given here were made by three investigators of varying degrees of experience in analysis who had no previous knowledge of the nature of the compounds. Chemical deductions from the interpretations were made by two of the analysts only. A high degree of unanimity was found between the separate interpretations, which were then compiled into a single report. These interpretations may be helpful in giving the reader who attempts this practice program in analysis some measure by which to judge the completeness of his work after each of the three steps. In these interpretations, the assignments which might be given to a band are listed in order of greatest likelihood as judged by the analysts *a priori*. Structures characterized by more than one band are identified by a brace about their grouped wavelengths in the *Bands* column.

Chemical Data

Plate Number	*Empirical Formula*	*Description*
6	$C_6H_5O_3N$	Yellow prisms, mp 113° C., v. s. hot water, alcohol, ether.
7	$C_7H_4O_3NCl$	Needle crystals, mp 94° C., soluble hot alcohol.
8	$C_{10}H_{10}O_3$	Acidic, mp 116° C.
9	$C_8H_9O_2N$	mp 256° C., v. sl. s. H_2O, alcohol.
10	$C_{15}H_{15}O_3N$	mp 76° C., prepared in sterol research.
11	$C_2H_4N_4$	
12	$C_8H_4O_3$	Crystalline, mp 131° C., v. sl. s. H_2O, s. alcohol, sl. s. ether.
13	$C_9H_8O_2$	Acidic, mp 133° C.
14	$C_{10}H_{12}O_4$	
15	C_8H_9ON	White solid, mp 113° C.
16	$C_6H_{10}O_3$	Liquid, 180° C., non acidic.

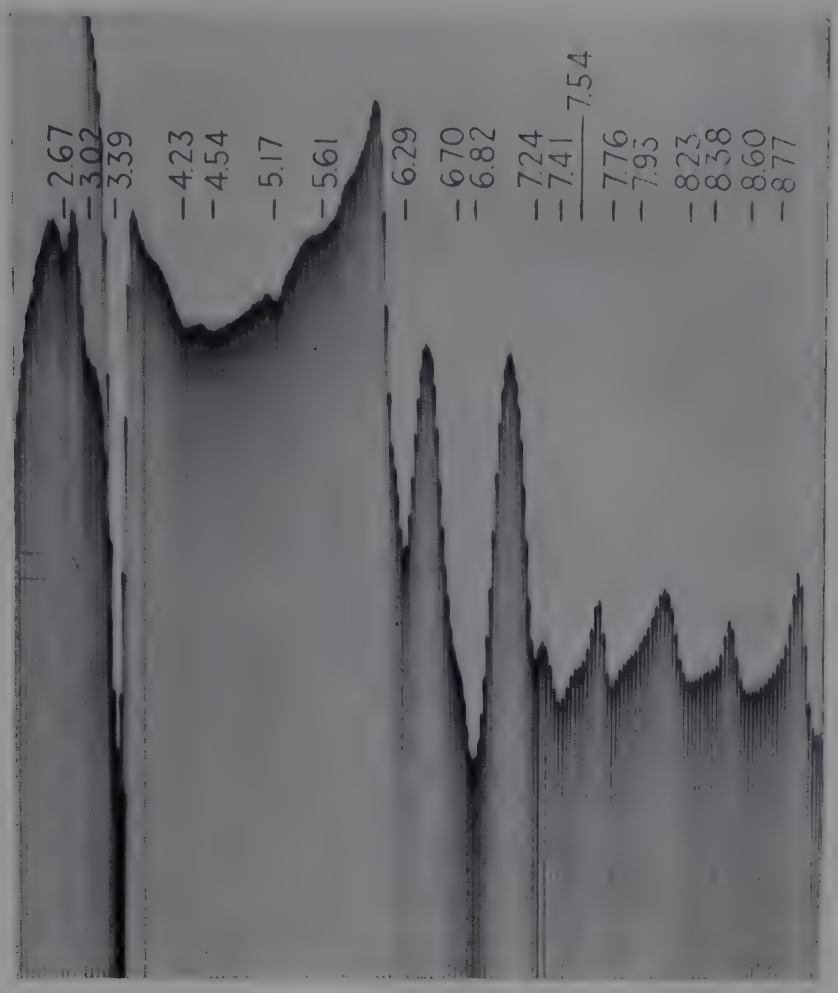


PLATE 6. Preparation: Nujol paste.

EXAMPLE 1

Plate 6

Band Observed	*Possible Assignments*	*Remarks*
3.02 μ	NH or OH	So weak that it is certainly from no more than one NH or OH group.
4.23, 4.54, 5.17, 5.61	Benzene ring vibrations	Phenyl compounds often show a series of low intensity bands in this vicinity.
6.2	Benzene ring vibration	Occurs as weak sidehill of 6.29 band.
6.29	C=N	
	CO_2^-	Not an amino acid CO_2^-
	st-a NO_2	Bands available for st-s at either 6.8 or 7.4. Wavelength is rather short for this, however.
	C=C	Probably too strong for this choice.
	NH_2	Supported by 3.02 band. Somewhat too strong.
6.70	Benzene ring vibration	

It seems highly probable that the benzene ring is present. The assignments of the 6.29 band are about equally likely. No carbonyl groups are possible other than the carboxylate ion.

Empirical formula: $C_6H_5O_3N$.

Description: yellow prisms, mp 113° C., vs hot water, alcohol, ether.

Assuming the benzene ring indicated above, which seems substantiated also by the small proportion of hydrogen, the absence of carbon bands makes it nearly certain that the oxygen atoms are on the nitrogen in a nitro group. The only explanation for the 3.02 band is now OH. The compound is a nitro phenol, on the basis of this reasoning.

Actual compound: p-nitrophenol.

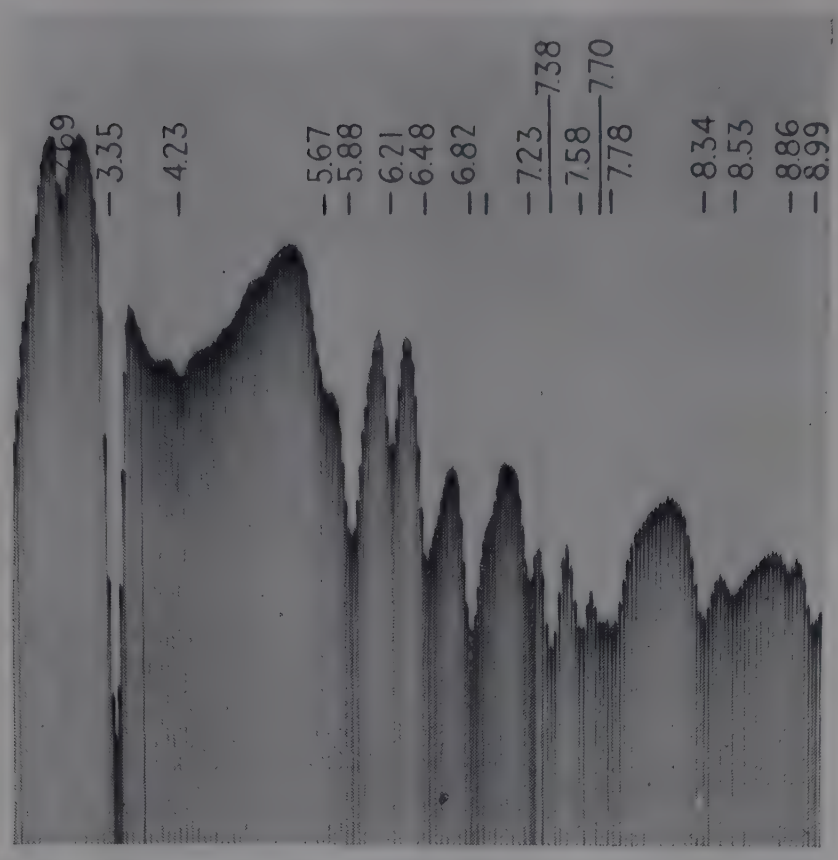


PLATE 7. Preparation: Nujol paste.

EXAMPLE 2

Plate 7

Band Observed	*Possible Assignments*	*Remarks*
4.23 μ, etc.	Benzene ring vibrations	Indicative.
5.67		Too weak to be essentially significant, phenyl, perhaps.
5.88	Ketone or aldehyde Conjugated ester Lactam *	Certainly a carbonyl.
6.21	Benzene ring vibration C=C	A little too intense.
6.48	NO_2	Not a combining band. Supporting st-s band at 7.38. Cf. p-nitrobenzoic acid.
6.6	Benzene ring vibration (2)	Occurs as weak sidehill of 6.48.

Empirical formula: $C_7H_4O_3NCl$.

Description: needle crystals, mp 94° C., soluble hot alcohol.

As in the preceding case, the small hydrogen content and bands observed indicate strongly a benzene ring. One oxygen atom is in a carbonyl group. The other two seem from the empirical formula to be best explained by the NO_2 group. Starting then with nitrobenzene, there are three remaining atoms to consider, one carbon, one chlorine, and one oxygen atom. Since the oxygen atom is located in a carbonyl group (probably aldehyde or ketone), a chlor-nitrobenzaldehyde suggests itself as the most probable structure, on the basis of the empirical formula and infrared spectrum.

Actual compound: p-nitrobenzoyl chloride.†

* Rather unlikely in view of the absence of NH at 3 μ.

† Conjugation has shifted the carbonyl band much farther than it is shifted in benzoyl chloride. Benzoyl chloride, however, has two bands in this region, one of which is of unknown origin. It has been customary to assign the band at 5.64 to this group, as being the more compatible with the normal position of other acid chlorides. In the light of this result, however, it is possible that the band at 5.77 is the proper choice.

Example 3

Plate 8

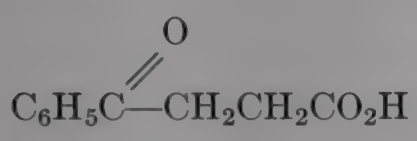
Band Observed	*Possible Assignments*	*Remarks*
3.57 μ, 4.26	Acid OH, bonded	
5.91	Acid C=O	Possibly conjugated. Band may be double, considering its intensity.
	Keto C=O	May be conjugated.
	Conjugated ester C=O	
6.27	C=C	About the right intensity.
	C=N	Too weak for this.
	Benzene ring vibration	Enhanced by conjugation or disubstitution. There is some indication of complementary absorptions at 4–5 μ, but the other characteristic absorptions are systematically concealed.
	N=N, CO_2^-, NO_2	Situated properly, but too weak to be seriously considered.

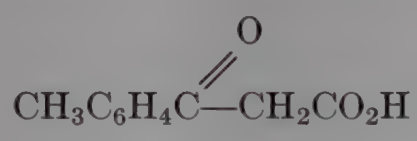
Empirical formula: $C_{10}H_{10}O_3$.

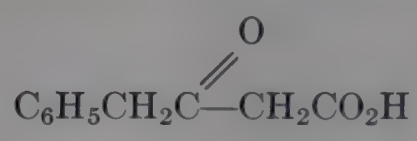
Description: acid, mp 116° C.

Since no alcohol type OH vibrations are observed, it is apparent that the oxygen atom which is not needed for the acid group, is present either as C—O—C or a carbonyl group. The latter probability is favored owing to the unusual intensity of the 5.91 band.

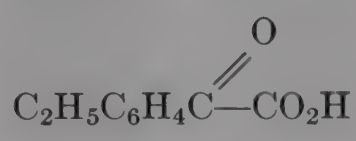
Assuming the presence of a benzene ring and a carbonyl group, one is led to suggest the following structures:

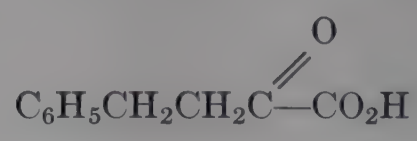




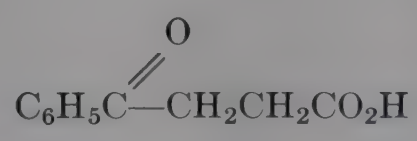


Other variants of this type of structure are also possible, and from studies of pyruvates, where the acid and ketone carbonyl bands were found to coincide, it is clear that these should also be considered.





Actual compound:



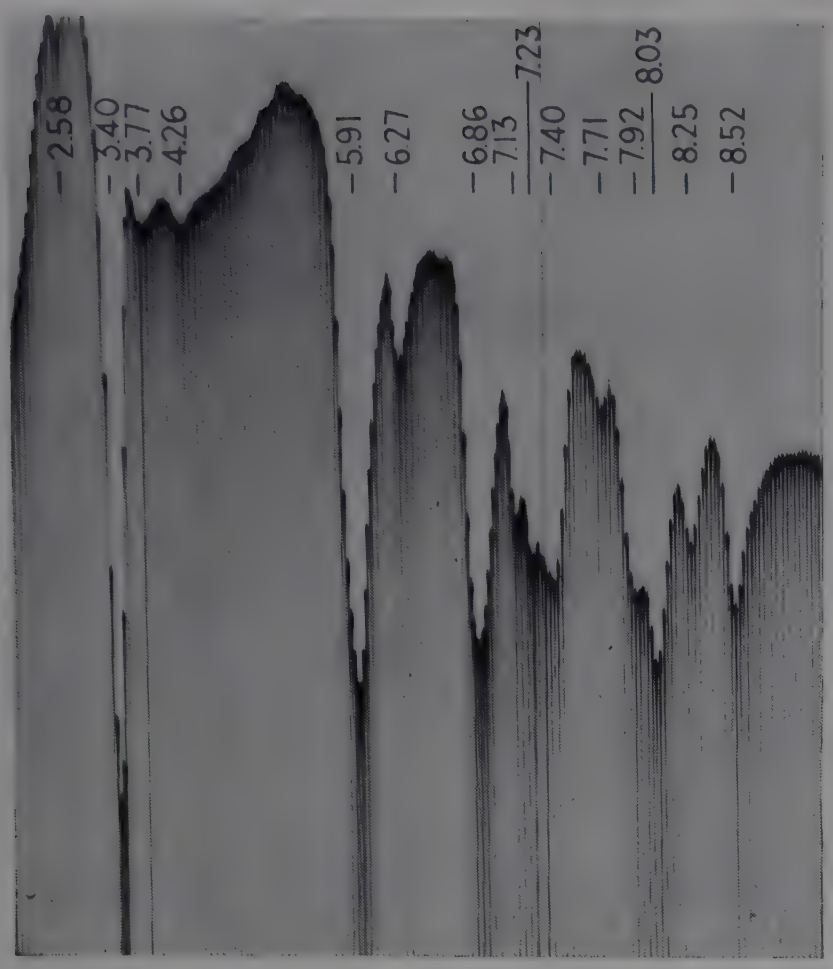


PLATE 8. Preparation: Nujol paste.

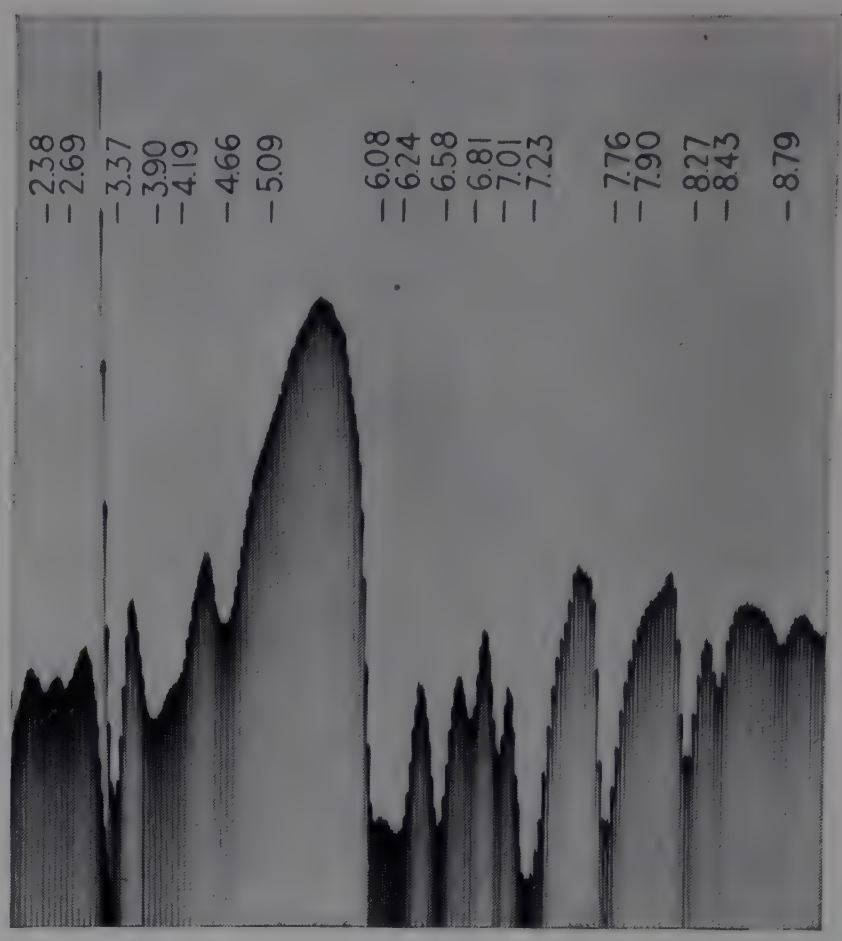


PLATE 9. Preparation: Nujol paste.

EXAMPLE 4

Plate 9

Band Observed	*Possible Assignments*	*Remarks*
3.90 μ		
4.19	4 μ bands of an aminoacid	
4.66		
6.08	Amino acid I	Alternative assignments can be made, but the whole spectrum seems without question to indicate an amino acid.
6.24	CO_2^-	
6.58	Amino acid II	

Empirical formula: $C_8H_9O_2N$.

Description: mp. 256° C., v. sl. sol. H_2O, alcohol.

NH_2 and CO_2H groups are indicated by the spectrum. This leaves a balance of C_7H_6. The small proportion of hydrogen immediately suggests a benzene ring, although there is no indication of it in the spectrum. It is, however, systematically concealed if present. A reasonable assumption is that the compound is either an amino-toluic acid, α-amino-phenyl-glycine, an aminomethyl-benzoic acid, an N-methyl aminobenzoic acid, an amino-phenyl acetic acid, or N-phenyl glycine. On the whole the spectrum indicates an NH_2 amino acid rather than an NH type. Comparison with the spectrum of N-phenyl glycine eliminates this compound.

Actual compound: p-amino-phenylacetic acid.

Example 5

Plate 10

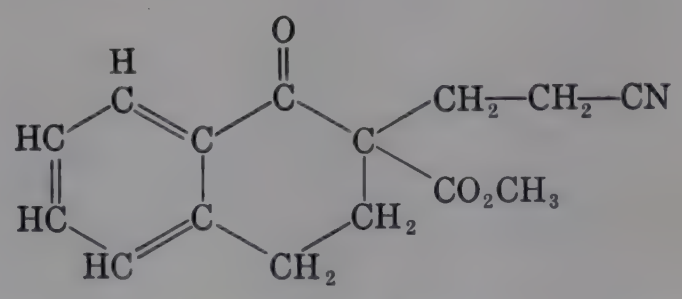
Band Observed	*Possible Assignments*	*Remarks*
3 μ		There is a slight indication of a sidehill at this point which is probably not significant.
5.39	C≡N	Long wavelength for this.
5.39, 5.65	Anhydride C=O	
5.39, 5.65, 5.89	Diacylimide	3 μ band should be much stronger to make this valid, unless the nitrogens are substituted. General intensity balance among bands unfavorable.
5.65	Ester C=O	Wavelength is short for a solid ester, but not prohibitive.
	Lactone C=O	If conjugated, would be equally valid with other choice.
5.89	Ketone C=O	Probably cyclic or else conjugated.
	Ester C=O	Conjugated.
	Lactam or urethane C=O	Must be N-substituted. Relatively unlikely, being a rare sort of compound.
6.27	C=C	
	C=N	Must be either cyclic or conjugated. Band is very weak for this choice.
	N=N	Limited possibility, owing to rarity.
6.27, 6.63	Benzene ring vibrations	Most likely choice, weak bands in 4–5 μ region seem favorable to this. 6.63 band is very weak compared with the 6.27 band so that a substituted phenyl ring is indicated rather than a conjugated ring.

Empirical formula: $C_{15}H_{15}O_3N$.

Description: mp 76° C., non-acidic, prepared in sterol research.

Comments on the structure cannot be extensively enlarged after knowledge of the empirical formula in this case. More knowledge is needed than is available from the limited evidence presented here. The most probable configurations are C≡N, an ester, a cyclic ketone and a benzene ring. This is purely a preference based on an intuitive comparison of the possibilities listed. *

Actual compound:



* The remarkable thing about the infrared method is the frequency with which intuition is correct. An examination of the actual structure shows that not only were all the outstanding features of the molecule proposed, they were exactly those which were intuitively selected as most probable.

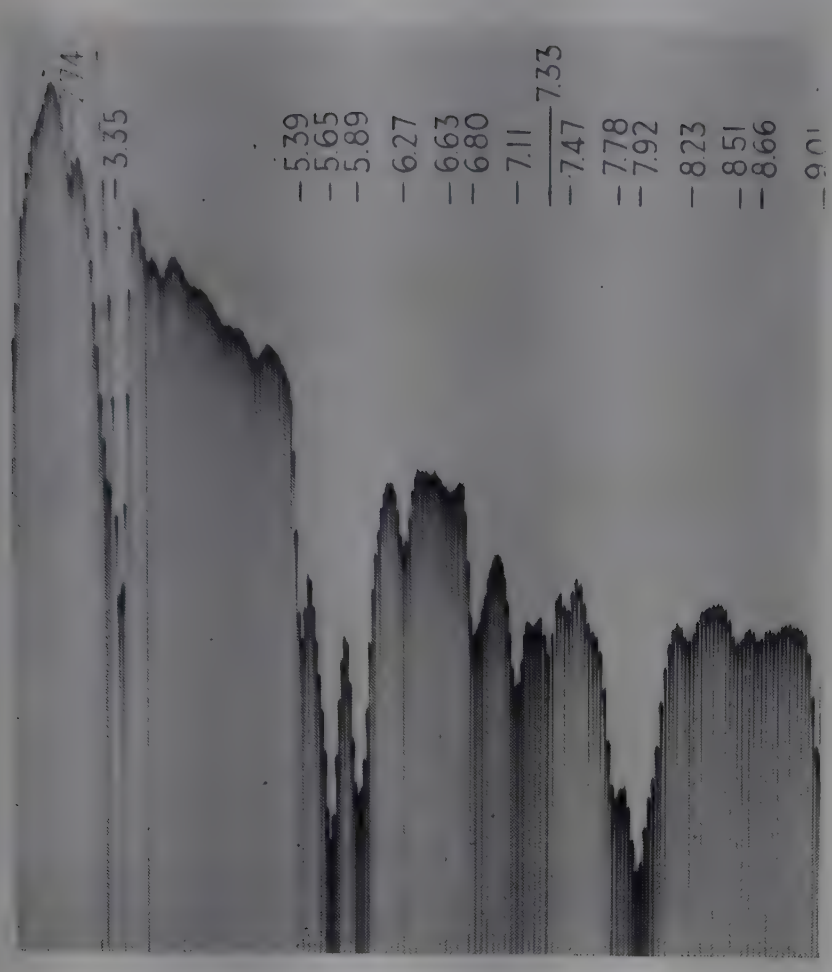


PLATE 10. Preparation: Nujol paste.

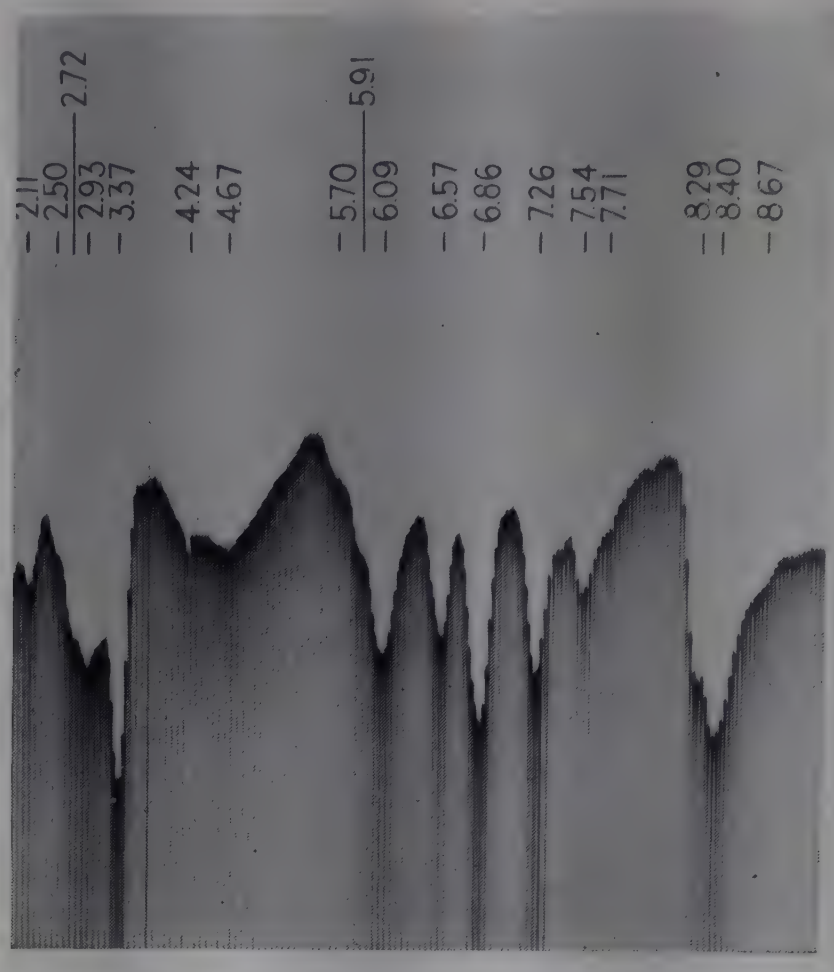


PLATE 11. Preparation: Nujol paste.

EXAMPLE 6

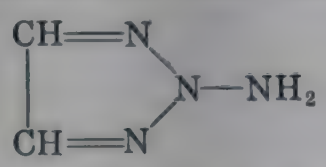
Plate 11

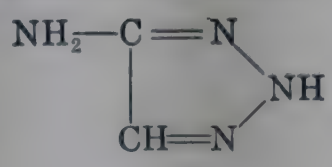
Band Observed	*Possible Assignments*	*Remarks*
2.93 μ	OH	The breadth of this band indicates that simple NH is unlikely.
	NH	Probably OH or NH_2.
4.24 }	Bonded OH	
4.67 }	Bonded NH	
	Phenyl	
5.91		Probably trivial.
2.93 }		
6.09 }	Amide	The sharp 3.0 μ band would have to be hidden in the broad 2.93 μ band. The three bands lack the distinctness of the usual amide bands. However, the intensity balance is quite normal for an amide.
6.57 }		
6.09	C=N	Too strong for C=C.
	NH_2	Rather strong and position is short for this group.
6.58	NO_2	The 6.86 and 7.26 μ bands appear to be normal oil bands, making the presence of a supporting st-s band unlikely.
	C=N	Conjugated in ring, as in some imidazoles.

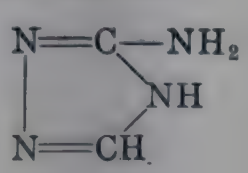
Empirical formula: $C_2H_4N_4$.

Before knowledge of the empirical formula is available, the presence of an amide group seems the most probable explanation of the observed spectrum. However, the empirical formula indicates that the 6.09 μ and 6.59 μ bands must be ascribed to conjugated and perhaps symmetric C=N and/or NH_2. The presence of NH_2 is definitely indicated by the complex band at 2.93 μ.

If then —C=N—C=N— and NH_2 are present, only a nitrogen and two hydrogen atoms remain to be fitted into the molecule. It seems probable that a ring structure is necessary. Possibilities are:







Actual compound: 4-amino-2,4,6-triazole.

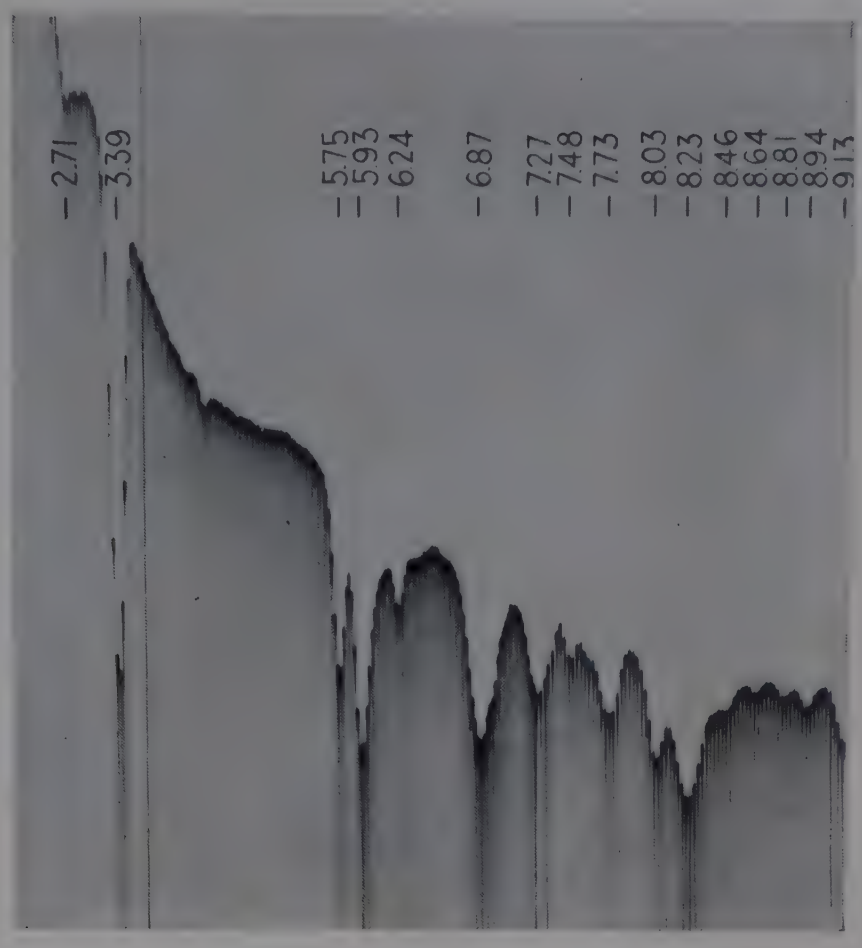


PLATE 12. Preparation: Nujol paste.

EXAMPLE 7

Plate 12

Band Observed	*Possible Assignments*	*Remarks*
5.75 μ	Ester C=O	
	Aldehyde or ketone C=O	
	Conjugated lactone C=O	
5.93	Ketone C=O	Cyclic or conjugated.
	Conjugated ester C=O *	
6.24	C=C	Conjugated.
	C=N	A little weak.
	Benzene ring vibration	Must be supported by very weak bands at 6.3 and 6.7 which were not measured. Probably doubly substituted.

Empirical formula: $C_8H_4O_3$.

Description: crystalline, mp 131° C., v. sl. s. water, s. alcohol, sl. s. ether.

The small amount of hydrogen indicates a ring compound, and the significance of the 6.24 band seems thus to be benzene. This leaves C_2O_3 which probably is arranged into an anhydride. The compound is probably phthalic anhydride. The normal symmetry splitting 5.75–5.93 μ found in anhydrides is present, together with a shift caused by the conjugation.

Actual compound: phthalic anhydride.

* This band was not assigned a *priori*.

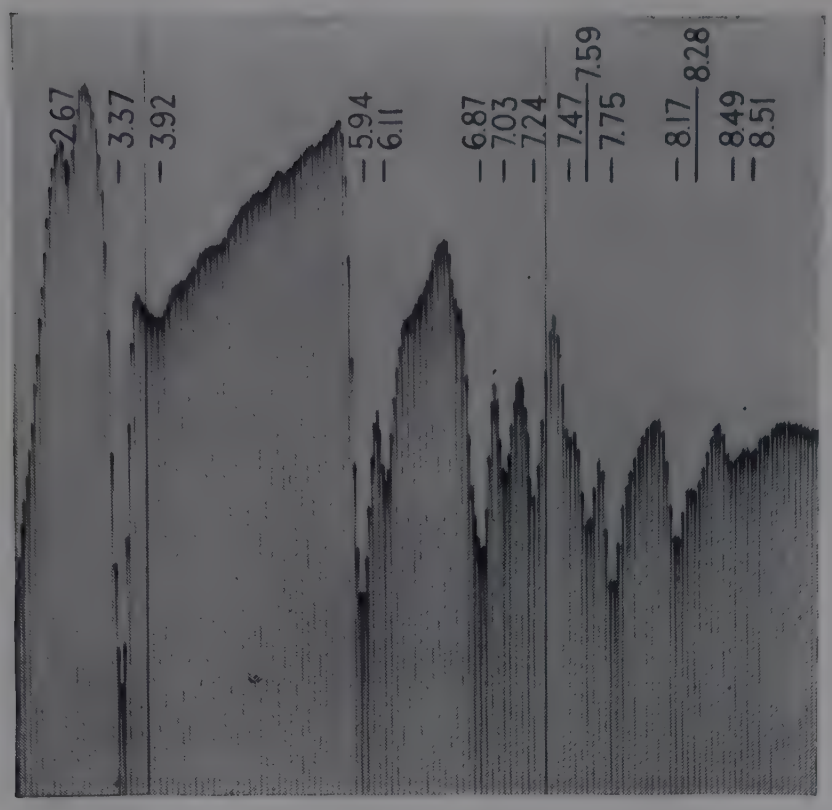


PLATE 13. Preparation: Nujol paste.

EXAMPLE 8

Plate 13

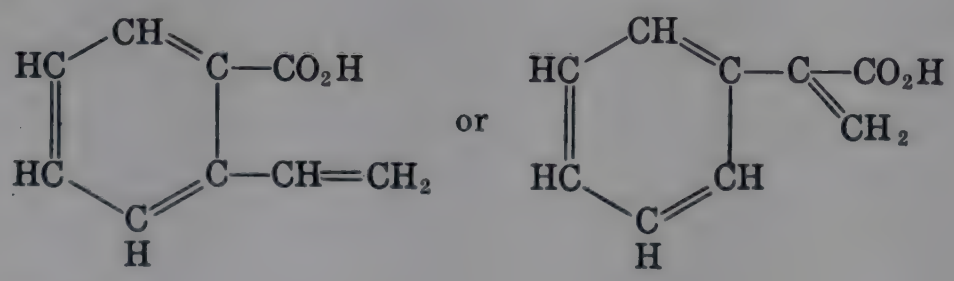
Band Observed	*Possible Assignments*	*Remarks*
3.92 μ	OH (bonded acid)	Highly probable.
	SH	Hardly sharp enough.
5.93	Acid C=O	Conjugated probably. N-acyl and ketone C=O are unlikely alternatives. The occurrence of the 3.92 band makes any other choice than acid C=O unattractive.
6.11	C=C	Conjugated?
	C=N	Cyclic?

Empirical formula: $C_9H_8O_2$.

Description: acidic compound, crystalline solid.

The presence of the ring structure which would be needed to explain the small proportion of hydrogen is indicated by bands not marked at 6.2 μ and 6.7 μ wavelengths.

Assuming the presence of a benzene ring group —CH=CH—CO_2H, the compound could be cinnamic acid. While this happens to be an excellent guess, several other less common structures would have been equally satisfactory in explaining the data at hand. Infrared data on CH frequencies would have been valuable to establish this compound unequivocally.



Actual compound: cinnamic acid.

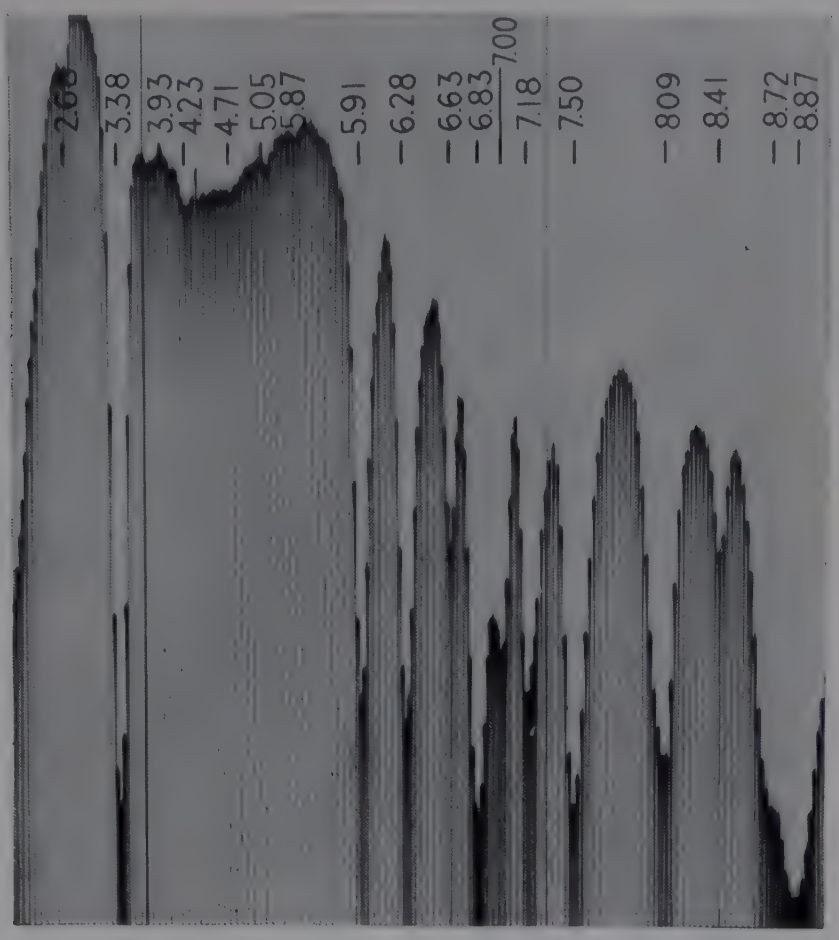


PLATE 14. Preparation: Nujol paste.

EXAMPLE 9

Plate 14

Band Observed	*Possible Assignments*	*Remarks*
5.91 μ	Ketone C=O	Conjugated? Band is certainly from C=O group.
	Aldehyde C=O	Conjugated?
	Conjugated ester C=O	
6.28	Phenyl vibrations	Enhanced * somehow.
6.63		Shift to 6.28μ indicates conjugated or substituted phenyl ring.
6.28	C=N, conjugated or cyclic	None of these alternative assignments seems very likely in view of the 6.63 band, which has such a high probability to be a phenyl band, that the 6.28 band must be attributed to the same source.
	CO_2^-	
	NO_2	
8.87	C—O—C	

Empirical formula: $C_{10}H_{12}O_4$.

The empirical formula contains a great proportion of oxygen. The spectrum showed no more than one carbonyl, unless the 6.28 band indicated a carboxylate ion, which seemed out of the question. It was probable then that the other three oxygen atoms occurred either as esters or ethers. This was in accord with the interpretation of the 8.87 band. A reasonable guess was that the compound was either a trimethoxybenzaldehyde, or a dimethoxy methyl benzoate. The latter choice is not in agreement with the position in which the ester absorption is found in methyl benzoate.

Actual compound: 3,4,5-trimethoxybenzaldehyde.

* Enhanced, it was subsequently seen, by the methoxy groups.

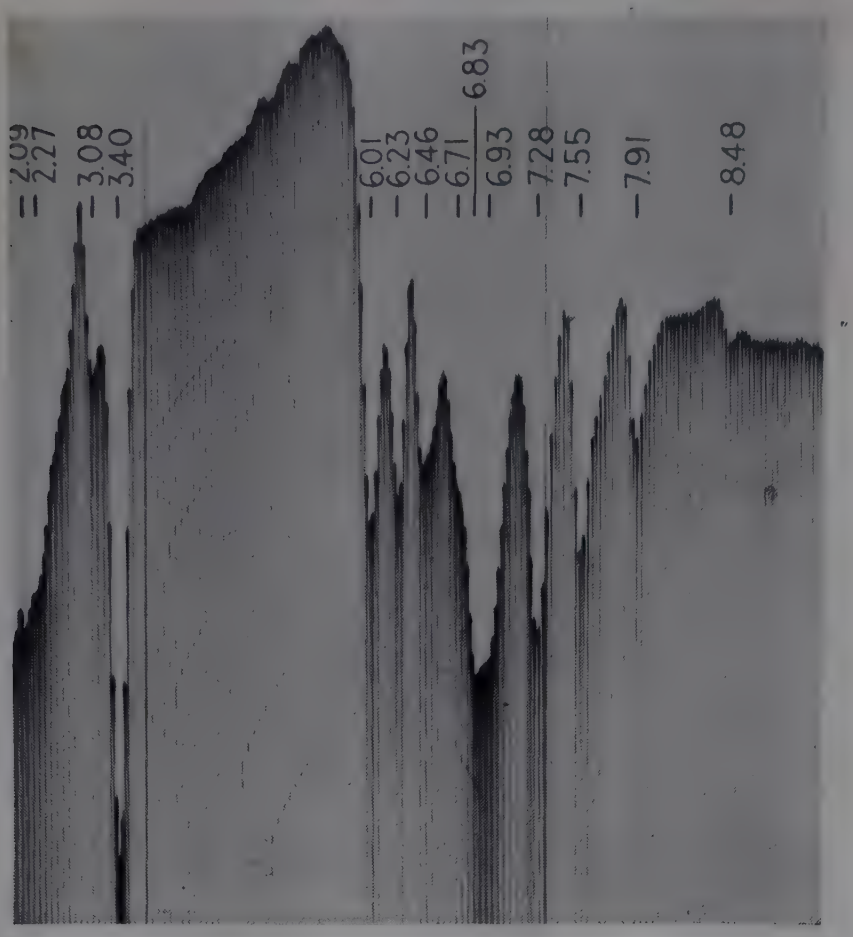


PLATE 15. Preparation: Nujol paste.

EXAMPLE 10

Plate 15

Band Observed	*Possible Assignments*	*Remarks*
3.08 μ	OH, NH	
6.01, 6.46	Amide group	Substantiated by 3.08 band.
6.01	C═N N-acyl C═O	Acyclic probably.
6.23, 6.70	Phenyl vibrations	Same argument as in previous example excludes other choice for 6.23 band, even though band is overly intense.
6.23	CO_2^- Conjugated or cyclic C═N	
6.46	NO_2	

A phenyl ring and an amide group are most likely to be present.

Empirical formula: C_8H_9ON.

Description: white solid, mp 113° C.

Position of the phenyl vibration's absorption at 6.23 μ indicates no conjugation. Compound containing amide group, phenyl ring, without conjugation, must be either acetanilide or N-formyl toluidine to fit formula.

Actual compound: acetanilide.

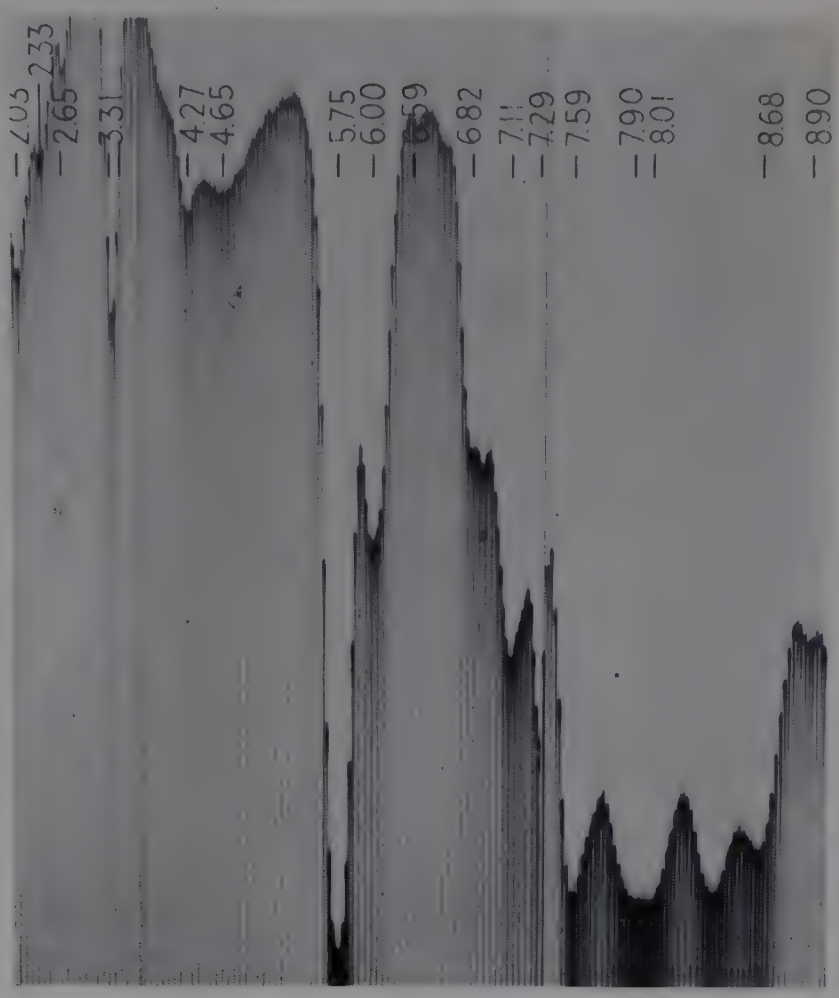


PLATE 16. Preparation: liquid in 0.015 mm. cell.

Plate 16

EXAMPLE 11

Band Observed	*Possible Assignments*	*Remarks*
5.75 μ	Ester C=O Ketone C=O Conjugated acid halide C=O	Intensity of band indicates possibility of two carbonyl groups unresolved.
6.05	C=C	Band is weak compared to spectrum in general, so C=C seems reasonable if band has any significance.

Empirical formula: $C_6H_{10}O_3$.

Description: liquid, bp 180° C., non-acidic.

One explanation which occurs to mind for the anomalous 6.05 band is the enol form of this compound, in which it could be C=C. This is unsatisfactory, first because the band is too intense to be accounted for by 4% of a compound containing a C=C, and second, because there is no corresponding OH absorption. Lack of evidence precludes any specific conclusions about structure in this case. Actually occurring groups have been predicted, however.

Actual compound: ethyl acetoacetate.

To conclude the discussion of methods of interpretation and the examples of this procedure, it seems necessary to call attention again to the general scope of the method and the limitations which have been imposed on it in this book. The spectral range between 2 and about 20 μ includes the absorptions corresponding to nearly all of the stretching vibrations of organic molecules, most of the bending vibrations of hydrogen however bonded, and some of the bending vibrations of the heavier components of the molecules. Only a limited number of types of vibrations absorb strongly, however. These are those of hydrogen, oxygen, and nitrogen. Vibrations involving carbon atoms alone are usually relatively weak.

The preoccupation evidenced in this book with the region from 2–7 μ and the single-bond vibrations of hydrogen and double-bond vibrations of nitrogen and oxygen should not carry the implication that this is the ultimate. This attitude was conditioned by the demands of the research program under which the bulk of the work was done. Strong bands, especially those of hydrogen, can be made of some use wherever they occur. Higher resolution than used here for the hydrogen vibrations in the 3 μ region is extremely helpful. It has been the intention of the authors to supply only some of the information and the methods by which a beginning may be made in the field of molecular structure analysis by use of infrared spectra.

Chapter VI

INSTRUMENTS AND EXPERIMENTAL TECHNIQUES

The foregoing discussions of structural analysis have made it clear that the regions of the spectrum which are most suitable for this work lie between 3 μ and 7 μ. Within these limits there are two short ranges of extreme importance. The first of these is the so-called double-bond region extending from 5.5 μ to 6.8 μ. The second is the locality immediately around 3 μ, where bands caused by the hydrogen-stretching vibrations are found. For the former, the modern prism spectrometer when fitted with a rock-salt prism possesses the required characteristics. That is, it has the resolution, speed of operation, and reproducibility of wavelength settings needed to yield satisfactory data for these analytical methods. When the sodium chloride prism is replaced by a lithium fluoride duplicate, the same spectrograph can serve acceptably in the 3 μ region also. Even better here, perhaps, is the grating instrument, since it can be accommodated to any desired resolution. In general, the instrumental demands of structural analysis are not excessive, and for many problems the information made available at 3 μ by the salt prism is adequate.

The Prism Spectrograph Recorder

This chapter contains a discussion of infrared spectrographs and some of the details of their operation. It will be illustrated at each point by reference to the recording spectrographs used in the research project at the University of Michigan, during the course of which most of the data for this book were obtained. Since all the spectra reproduced in this book were recorded on one particular instrument it is appropriate that it should be described at some length and that only brief mention be made of the other spectrograph used.

The basic features of this instrument [17] are given in Figure 6–1. The source was a Nernst filament carrying 0.65 amperes on a 220-volt a-c line with voltage-regulation. A metal or mica shutter, driven by a synchronous motor geared to give the shutter a period of 3.33 seconds, was used to interrupt the optical beam. A KBr window separated the source box from the spectrograph so that each could be evacuated separately. The bilateral slits were 2.5 cm long, the entrance slit being curved to compensate for the curvature otherwise found in the final image. The slits were closed automatically by a gear train used in conjunction with the mechanism of the prism drive. This was done to correct partially for the emissivity spectrum of the glower and irrationality of dispersion of the prism. Variation in the rate of closing was accomplished by the choice of suitable gear ratios. It was nearly always possible to find a ratio which gave a fair approximation to constancy of energy entering the spectrograph at all wavelengths, irrespective of the nature of the sample.

The main collimating mirror was an off-axis paraboloidal mirror of 50-cm focal length. The prism mounting was of the Wadsworth-Littrow type. The plane Wadsworth mirror was mounted adjacent to the prism on the prism table, the plane Littrow mirror remaining fixed. This arrangement served to use the prism twice, and at the same

[17] H. M. Randall and John Strong, *Rev. Sci. Instr.* **2**, 585 (1931). This spectrograph underwent many modifications during the fifteen years preceding this present monograph but the optical path remains much as originally designed.

time permitted any beam of light which fell on the thermopile to traverse the prism approximately at minimum deviation, regardless of wavelength. An ellipsoidal mirror having focal lengths in the ratio of 1:5 was used to image the exit slit upon the thermopile receiver.

It has been established that, for this spectrograph, the readings of a revolution counter, geared so that a change of one unit indicated a rotation of the prism table through one second of arc, are more reliable than are the readings of the divided circle, which it has accordingly replaced. In the discussion following, the angular rotation of the prism table will generally be expressed in revolution counter numbers or veeder numbers,[18] one veeder number being the equivalent of one second of arc of prism table rotation.

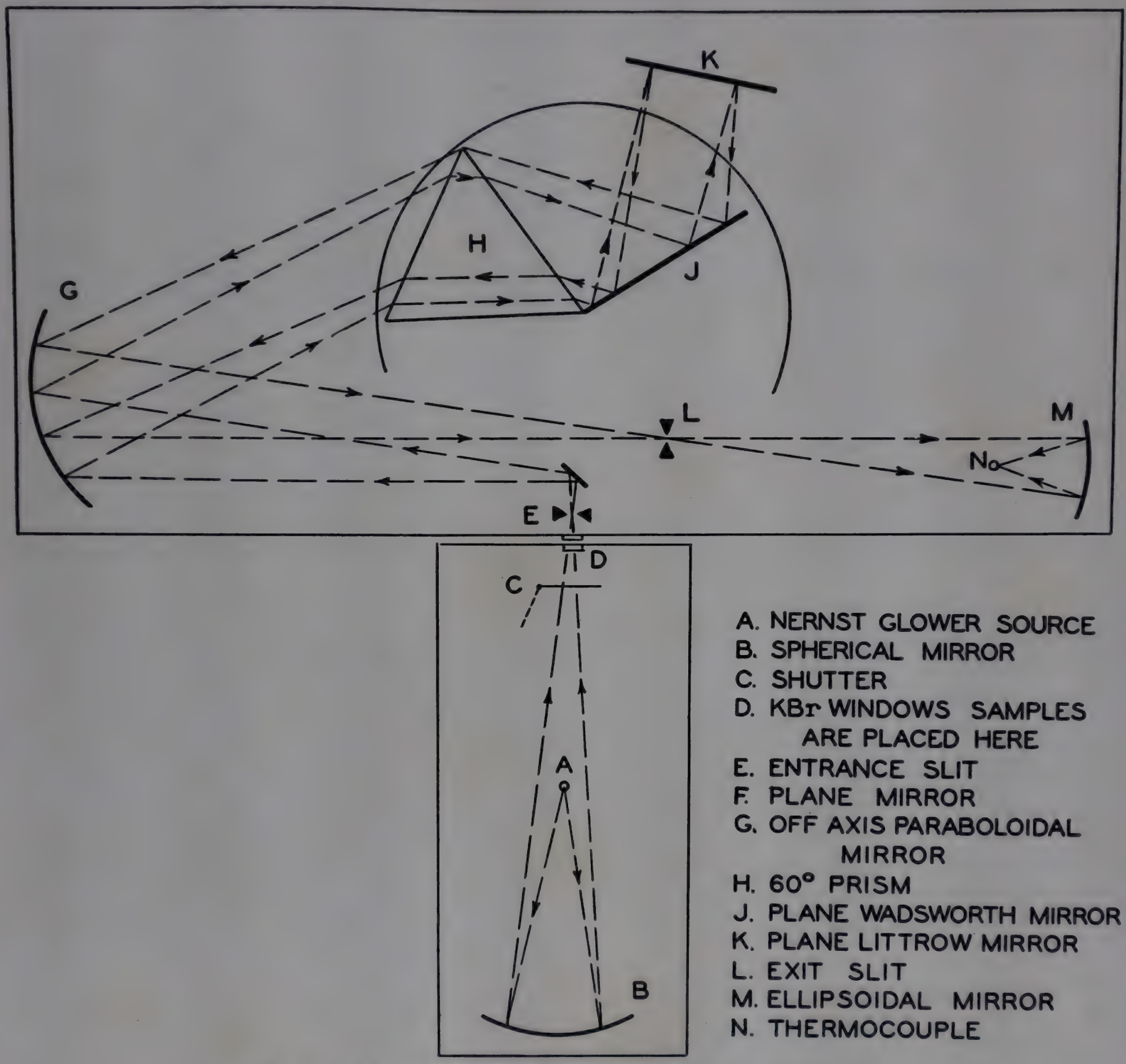


FIG. 6–1. Schematic diagram of the optical path of the prism spectrograph.

The major portion of the work, covering the 2–15 μ region, was done with a 60° sodium chloride prism with sides 10 cm long and 8 cm high. Sup-

[18] The revolution counters were made by the Veeder Company, hence the name.

plementary work in the 14–24 μ region required a potassium bromide prism, the one used having sides 7 cm square and a refracting angle of 60°. To obtain high resolution in the 3 μ region, a lithium fluoride prism was first used, but the desired resolution was subsequently obtained with a grating instrument.

The type of thermopile used has been described by Strong.[19] The particular thermopile used in this spectrograph had a total resistance of 35 ohms when its two junctions were connected in series. It was evacuated separately from the spectrograph case. Shielded cables connected the thermopile to a galvanometer which served as the primary galvanometer in a Firestone [20] periodic amplifier. The amplifier output operated a secondary galvanometer whose motion was observed and recorded. The galvanometers were both low-resistance instruments with sensitivities of approximately 0.4 microvolts per millimeter at a scale distance of one meter, the primary having a period of 2 seconds and the secondary of 1 second.

Recording was accomplished by replacing the ordinary galvanometer scale with a sheet of photographic paper on a rotating drum geared to the prism drive. A short-focus cylindrical lens across the full width of the paper served to focus the galvanometer beam into an intense point of light. Since the individual swings of the galvanometer, back and forth about its zero position, are proportional to the instantaneous transmission of the sample, the envelopes of the two termini of the swings form a double record of the absorption spectrum of the sample. Only one half of this double record is shown in the reproductions of spectra in this book.

Energy Considerations

Brownian motion [21] in the thermopile-galvanometer system was computed to produce a signal of 1×10^{-9} volts. The noise level experimentally observed was about three times as great, being about 3×10^{-9} volts. The amplifier gain was adjusted to cause a 1-millimeter zero-point fluctuation of the recording light beam on the photographic drum. Full-scale deflections were produced in this case by signals of approximately 0.4 microvolts. The amplification factor of the periodic amplifier was about 1:75, higher gains being of little advantage because of the proportionately increased raggedness of the records obtained.

Sensitivity of an energy-measuring system may be defined [22] to be the intensity of radiation which can be measured in a given time with a given accuracy. Using this definition, the time interval being taken as one period of the shutter (3.33 seconds) and the desired accuracy being such that the deflection will have a mean relative error of 1 per cent, the prism spectrograph under operating conditions, with slitwidth and resolution as described below, had a theoretical sensitivity of 6×10^{-9} watts (i.e., radiant power of 0.06 ergs per second incident upon the thermopile receivers during each period of the shutter was computed to generate an electromotive force of 3×10^{-7} volts in the thermopile circuit; the resulting 100-millimeter deflection could be measured accurately to within a millimeter).

Resolution and Slitwidths

Studies of the fine structure of the CO_2 band at 15 μ and the NH_3 band at 11 μ show that lines 0.034 μ (3 cm^{-1}) apart were just resolved. At 4 μ, the resolution was about the same when expressed in wavelength (0.03 μ) but corresponds to a frequency separation of about 20 cm^{-1}. For the work done in this research such high resolution was rarely needed.

Table 6 lists the effective slitwidths used at different regions of the spectrum. Effective slitwidth is here defined as the wavelength separa-

TABLE 6. EFFECTIVE SLITWIDTHS OF PRISM SPECTROGRAPH

Wavelength Region	Slitwidth			
	s Linear, mm	Angular (vee. no.)	Effective or Spectral	
			μ	cm^{-1}
3 μ (3330 cm^{-1})	0.04–0.08	4.1– 8.2	0.012–0.023	13. –26.
6 μ (1667 cm^{-1})	0.09–0.13	9.3–13.4	0.015–0.021	4.4– 6.0
10 μ (1000 cm^{-1})	0.24–0.30	24.8–31.0	0.025–0.030	2.5– 3.0
15 μ (667 cm^{-1})	0.40–0.60	41. –62.	0.02 –0.03	0.9– 1.3

[19] John Strong, *Procedures in Experimental Physics*, p. 305, Prentice-Hall, 1938.

[20] F. A. Firestone, *Rev. Sci. Instr.* **3**, 162 (1932).

[21] Gustaf Ising, *Phil. Mag.* **1**, 827 (1926); F. A. Firestone, *Rev. Sci. Instr.* **3**, 162 (1932).

[22] John Strong, *op. cit.*, pp. 333–337; C. H. Cartwright, *Physics* **1**, 211 (1931).

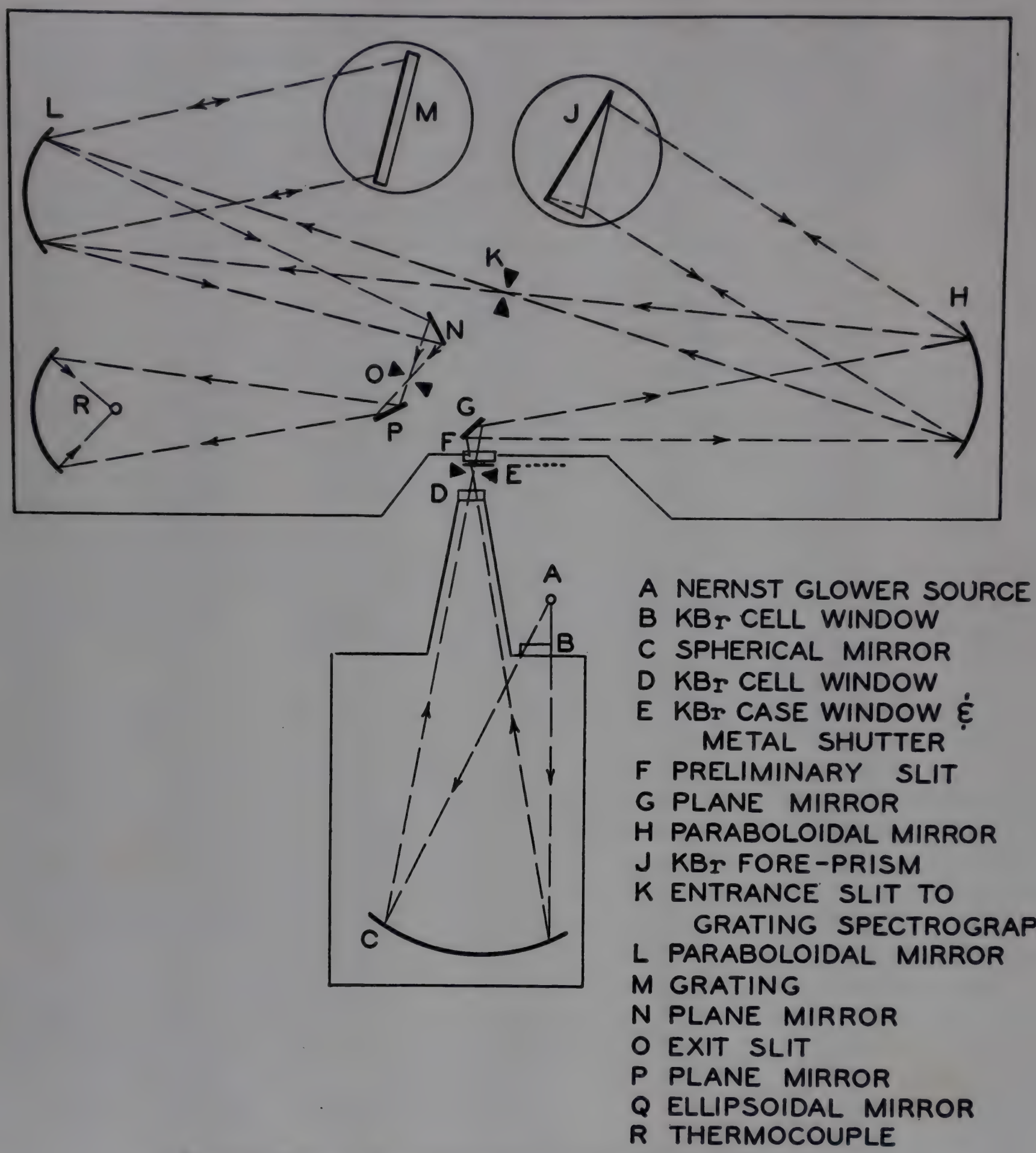


FIG. 6–2. Schematic diagram of the optical path of the prism-grating spectrograph.

tion between the two rays whose maxima fall on either edge of the exit slit. For the particular optical arrangement of the Randall-Strong spectrograph the angular displacement $\Delta\theta$ of the prism required to replace the one ray by the other is related to the focal length F and the exit slit-width s by the expression

$$\Delta\theta = ks/4F$$

where the proportionality constant $k = 1$ radian/cm $= 2.06 \times 10^4$ veeder nos./mm.

The Prism-Grating Spectrograph

The infrared prism-grating spectrograph[23] is still used largely as a tool for pure research and has not as yet, to any great extent, followed the infrared prism spectrograph into the industrial research laboratory. This type of instrument is merely a grating spectrograph in which the overlapping of spectral orders produced by the grating alone is eliminated by introducing a "fore-

[23] H. M. Randall, J. Appl. Phys., 10, 768 (1939).

prism" into the optical path to act as a rough monochromator. The prism-grating spectrograph is indispensable in problems where the highest dispersion and resolution are required; in all other cases, prism spectrographs are preferred because of their simplicity and rapid performance. The grating spectrograph may be calibrated either from strictly geometrical considerations or by comparison of spectra.

A diagram of the prism-grating spectrograph used in this research work is given in Figure 6–2. Two gratings, ruled by the University of Michigan ruling engine, were used. These gratings had 1200 and 4800 lines per inch, respectively. The main contribution of this spectrograph came in studying the 3 μ region under high dispersion with the 4800 lines per inch grating. A comparison of Table 6 and Table 7 will show that this grating, under operating conditions had roughly three times the dispersion of the rock-salt prism at 3 μ. The grating constants of this spectrograph were determined by measuring the location of 6 lines of water vapor at 6.4 μ, using wavelength values as determined by Plyler and Sleator.[24]

Table 7. Effective Slitwidths of the Prism-Grating Spectrograph When the Grating Ruled with 4800 Lines/Inch Is Used

Wavelength Region	Slitwidth		
	Linear, mm	Effective or Spectral	
		μ	cm^{-1}
3 μ (3330 cm^{-1})	0.35–0.50	0.0035–0.005	3.8–5.5
6 μ (1667 cm^{-1})	1.0	0.009	2.5

Calibration of Prism Spectrographs

Spectrographs may be calibrated in a number of ways with essentially the same result. One method makes use of the geometry of the optical system and the dispersion curve[25] of the prism. An empirical method of calibration is possible by comparing prism and grating spectra.

Calibration by Known Absorptions

While the dispersion of a sodium chloride prism is good between 5 μ and 15 μ, it is relatively poor between 2 μ and 5 μ. The accuracy of calibration in these two regions for a salt prism varies accordingly. In the shorter wavelength region ten lines from the spectra of mercury vapor, ammonia, carbon dioxide and methyl chloride are useful as calibration wavelengths. The grating measured wavelength values of these 10 absorption bands are listed in Table 8.

Table 8. Calibration Wavelengths in the 2–5 μ Region for the Sodium Chloride Prism

Material	Wavelength, μ	Reference
CO_2.....	4.225	E. F. Barker, *Astrophys. J.* **55,** 391 (1922)
CH_3Cl.....	3.473	Bennett and Meyer, *Phys. Rev.* **32,** 902 (1928)
	3.370	*Ibid.*
NH_3.....	3.098	Robertson and Foy, *Proc. Roy Soc.* **120,** 163 (1928)
	2.998	*Ibid.*
	2.916	*Ibid.*
CO_2.....	2.765	Barker, *op. cit.*
	2.688	*Ibid.*
NH_3.....	2.264	Robertson and Foy, *op. cit.*
Hg arc.....	1.970	*Handbook of Chemistry and Physics*

In order that records from the two types of instrument shall be fully comparable the prism and grating spectrographs need to have the same resolution, when there will be a one-to-one correspondence between the absorptions appearing in the two spectra. By properly adjusting the resolution of a grating instrument, Oetjen, Kao and Randall[26] succeeded in fulfilling this condition for the fine structure lines of the bands of carbon dioxide (13.8–15.4 μ), ethane (11.9–12.4 μ),

[24] E. K. Plyler and W. W. Sleator, *Phys. Rev.*, **37,** 1493 (1931).
[25] Paschen has obtained refractive indices for NaCl and KCl. Ann. der. Phys., 26, 120 (1908).
[26] R.A. Oetjen, Chao-Lan Kao, and H. M. Randall, *Rev. Sci. Instr.* **13,** 515 (1942).

ammonia (7.9–14.0 μ) and water vapor (5.0–7.9 μ). For this comparison, these four gases furnish 164 sharp lines quite uniformly spaced between 5 μ and 15 μ. The lines as measured on the grating instrument are certainly accurate to 0.001 μ. Thus, exact calibration of a salt prism instrument in the longer wavelength region in terms of fundamentally measured grating wavelengths is possible.

Reproducibility of Spectra; Corrections to Be Applied

To justify such a calibration, it is essential that the prism instrument be able to repeat settings on sharp absorption lines with a corresponding accuracy. Repeated trials have shown that the positions of sharp lines can indeed be determined with sufficient accuracy, i.e., to within one or two veeder numbers, provided certain definite conditions of observation are followed. These conditions require for one thing that the temperature of the prism be constant or be corrected for if it is variable;[27] for another, that the speed of operation be suitably slow and remain constant or be corrected for if greater than a certain low value.[28] Associated with these two conditions (as well as with slight mechanical shifts to be mentioned later) is the accuracy with which the spectrograms permit the location of the absorption maxima in terms of veeder numbers.

The degree of accuracy required and the detail desired in the spectrogram determine the proper rate of recording. For greatest accuracy and detail, it is essential that the recording show a minimum of distortion in the contours of the absorptions when compared with the corresponding ones of the grating instrument. When the entire spectrum, 2–15 μ, was run in 1½ hours,[29] a fairly high degree of accuracy was obtained. Under these circumstances there were between 3 and 4 swings of the recording galvanometer in the time required to record two successive fiducial lines. (Fiducial lines were automatically flashed onto the photographic record paper every 30 veeder numbers and provide a one-dimensional grid to assist in measurement.) With 3 or 4 swings per fiducial line, it is possible to repeat the location of sharp lines to within 3 to 5 veeder numbers. Highest accuracy was obtained when the spectrum was covered in 6 hours by turning the prism four times as slowly while at the same time changing the gearing between the prism drive and recording drum drive so that the drum rotated relatively more rapidly. This enabled the spectrum to be spread out so that all the detail could be seen on the record. On these 6-hour records there are about 14 galvanometer tracings between fiducial lines and, under these conditions, experience shows that sharp lines may be repeatedly located within 1 or 2 veeder numbers.

Further refinement appeared fruitless as there were erratic shifts from time to time of this same order of magnitude. These seemed to arise from mechanical sources. It is necessary to check for such shifts by frequent measurement of certain standard lines. Over 6 months of severe operation, these changes never exceeded ±3 veeder numbers (±0.006 μ at 4.225 μ, the wavelength of the carbon dioxide doublet used for checking the calibration). These shifts were within the limits of accuracy required for the major portion of this sort of work, and were accordingly ignored.

Calibration Curve for Most Accurate Work

It is possible to construct a large-scale calibration curve for the prism spectrograph which preserves the accuracy of measurement just described using the 164 lines from the 4 bands in the 5–15 μ region, and the 10 lines in the 2–5 μ region. The accuracy is about ±0.001 μ at 15 μ, ±0.005 μ at 5 μ, and ±0.01 μ between 2 μ and 3 μ. The

[27] By altering the temperature of the room through a sufficient range it was established, after temperature equilibrium was attained, that a rise in temperature of the salt prism of 1° C. resulted in a shift in the position of absorption lines of 5 veeder numbers (roughly 0.01 μ) toward longer wavelengths in the spectral region between 3 μ and 13 μ and of 4 veeder numbers (roughly 0.003 μ) in the 13–15 μ region.

[28] Tests showed that the shifts in the positions of lines due to varying speeds of drive were proportional to the speeds employed. This shift resulted from a lag in response of the thermopile and recording system behind the instantaneous position of the prism. It was twice as large for the envelope of swings (or record) photographed during the "shutter closing" cycle as for that photographed during the "shutter opening" cycle. This is an effect to be watched for in a recording system which employs a low frequency shutter and a periodic amplifier. The angular magnitude of this lag (for the "shutter-opening record") proved to be, for this instrument, numerically equal to the veeder numbers driven through in about two-fifths of a period of the shutter (i.e., in 1.4 sec).

[29] The 1½-hour record and the 6-hour record (referred to later) result in angular lags of 2 veeder numbers and 0.5 veeder numbers respectively. Translated into wavelength, at 5 μ for example, these lags shift the absorbing minima by 0.004 μ and 0.001 μ and a "speed correction" must be applied accordingly.

above estimated accuracies in both ranges, 2–5 μ and 5–15 μ, correspond to ± 2 veeder numbers throughout. The spectral range with the rock-salt prism can be covered in 12,500 veeder numbers, i.e., by an angular rotation of the prism of about $3\frac{1}{2}°$ of arc.

Calibration Curve for Spectra Recorded in This Book

In this research each complete spectrum, 2–15 μ, was usually run off in about one half hour, the prism table being rotated at 4 different speeds, most rapidly at long wavelengths where the dispersion is large and the absorption bands are farther apart, and most slowly at the shortest wavelengths where the dispersion is poor and the bands correspondingly crowded together on the photographic record. Under these conditions of rapid recording the number of galvanometer tracings outlining each absorption band (i.e., the number of swings per fiducial line) was so reduced that the position of the line could not be determined to closer than ± 0.01 μ.[30] This accuracy, however, was all that was required in such a survey study of organic compounds. Accordingly, the use of the large-scale calibration curve became needlessly cumbersome and it was replaced by its projection in the form of a scale reading directly in tenths of microns and permitting accurate estimation to hundredths of microns.[31] Tests on the reproducibility of wavelength measurements using this rapid recording and measurement with the scale showed that in no instance did individual measurements fall outside ± 0.02 μ of the mean value determined for each absorption line, and more than 90 per cent fell within ± 0.01 μ of the mean.[32]

[30] This uncertainty is, of course, independent of the "speed shift" (see footnote 28) for which a correction was made. Although the angular lags at the four different speeds were, of course, different, they were equivalent to approximately 0.01 μ wavelengths shift throughout the spectrum. This "speed correction" was made, accordingly, for all the "half-hour records" (see footnote 29).

[31] A number of these scales were simultaneously produced by allowing the automatic flasher to place the fiducial lines at regular 30 veeder number intervals while at the same time manually flashing the tenth micron lines onto the photographic paper at the appropriate veeder numbers.

[32] The 3.35–3.55 μ absorption caused by C—H stretching vibrations, and due largely to the paraffin oil in which the samples were suspended, is so deep and broad (about 0.1 μ wide at the bottom) that its position is indeterminate to about 0.03 μ. Measurements of this band were accordingly not included in the reproducibility tests.

Secondary Calibration Methods

Should the use of the four gases for calibrations be inconvenient, the liquids in the accompanying table, Table 9, have spectra which are very well suited for many calibration purposes not requiring extreme accuracy. These liquids, cyclic organic compounds, are easily obtained in the pure form and involve only routine, liquid-sample preparation for spectrum analysis.

TABLE 9. SUPPLEMENTARY CALIBRATION COMPOUNDS

Compound	*Cell Thickness, mm*
Benzene	0.02 and 0.15
Pyridine	0.01
Thiophene	0.01
Dioxane	0.04
Pyrrole	0.01
Benzothiazole	0.02
2-Methyl benzothiazole	0.02
Benzoxazole	0.02
2-Methyl benzoxazole	0.02

Reproductions of spectra with wavelength values to the nearest hundredth micron are to be found for all the above compounds in the catalogue of spectra. However, more accurately determined spectra for the first three compounds, benzene, pyridine, and thiophene, were obtained. Their wavelength values are made available in Table 10 for easy comparisons of calibrations. Each of these compounds may be used separately for calibration purposes but it should be noted that the spectra of all three supplement each other well. Furthermore, when the 3 μ lines of benzene (0.15 mm thick) are added to them and likewise the 10 μ lines of benzoxazole (0.02 mm thick) and the 13 μ and 14 μ lines of benzothiazole (0.02 mm thick), there is a very good coverage of the whole 2.5–15.0 μ region with approximately 70 usable lines.

When the wavelengths in Table 10 are given to two decimal places they are accurate to about ± 0.02 μ in the 2–5 μ region, and ± 0.01 μ in the 5–15 μ region. When given to three decimal places, they are accurate to about ± 0.01 μ in the 2–5 μ region, ± 0.007 μ in the 5–9 μ region and ± 0.004 μ in the 9–15 μ region. This is only a rough indication of accuracy—sharp, single lines, indicated by "$\star$", being more accurately deter-

TABLE 10. BEST VALUES OF CYCLIC CALIBRATION COMPOUNDS

Benzene (0.02 mm)		Pyridine (0.01 mm)		Thiophene (0.01 mm)	
μ	%	μ	%	μ	%
2.43	10	2.414	10	2.514	5
3.272	25	*3.278 [a]	20	2.596	5
*3.312	60	3.320 [a]	30	*3.226	25
4.307	10	5.023	10	4.611	5
4.523	10	5.204	10	5.545	10
*5.104	30	5.353	10	5.657	10
*5.520	40	5.931	10	*6.284	30
*5.815	15	6.107	10	6.417	20
6.332	10	6.260	30	*6.588	30
*6.549	15	*6.325	75	*7.112	75
*6.768	90	*6.743	25	7.779	10
*6.951	15	*6.962	75	*7.987	90
*7.188	25	7.294 [b]	10	*9.250	75
8.488	15	*8.213	25	*9.665	75
8.713	10	*8.715	25	11.06	5
*9.645	75	*9.360	25	11.475	20
10.09	10	*9.702	50	*11.98	100
11.76	10	*10.092	50	13.82 [a]	100
12.91	10	*13.345	75	14.07 [a]	100
13.39	10	14.18 [c]	75	16.6 [d]	30
14.2	10	16.9 [d]	75	22.2 [d]	40
		19.2 [d]	10		

SUPPLEMENTARY (REGIONS POORLY COVERED BY THE ABOVE COMPOUNDS)

Benzene (0.15 mm)		Benzoxazole (0.02 mm)		Benzothiazole (0.02 mm)	
3.43	10	*9.97	75	*12.06	40
3.53	10	10.24	10	*12.52	75
3.77	10	*10.69	30	*13.15 [e]	100
3.86	10	*10.87	75	*13.72 [e]	100
				14.17	40
				14.98	40

[a] Not completely resolved.
[b] Partly obscured by the background.
[c] A very broad line.
[d] Use the 0.15 mm cell thickness.
[e] Should be obtained with thinner cell to give 50 to 70% absorptions.

mined, and broad lines or "shoulders" being less accurately determined. Percentage absorptions given in the table are only rough estimates. The values given above 15 μ by the KBr prism are approximate only.

PREPARATION OF SAMPLES FOR SPECTROSCOPIC ANALYSIS

To obtain the spectrum of any given compound it is necessary so to process the material that it can be spread out in a uniform, thin layer and be interposed in the optical path. Radiation leaving the source passes through the sample layer before reaching the entrance slit. There are many methods of sample preparation in use as well as a large variety of sample holders. The following discussion of equipment and methods of sample preparation used in obtaining the spectra reproduced in this book will serve to illustrate this variety.

Notes on Apparatus

Solid samples whose spectra were desired in the 2.5–15.5 μ region were mounted on sodium chloride plates, while potassium bromide plates were used for this purpose when the 14–24 μ region was studied. These plates were about 1 × 4 cm in area, and 3 mm thick. Made from either natural or synthetic crystals, they were cut with faces approximately parallel, then highly polished. As it was necessary to use the same plates over and over again, they were carefully cleaned and repolished between operations. In a few instances, silver chloride plates were used when it was desirable to evaporate the solid sample from a water solution. These silver chloride plates were satisfactory over the whole 2.5–24 μ range studied.

Polishing the plates brought out some peculiarities in the abrasives available. Both ferric oxide (red rouge) and titanium oxide (white rouge) have absorptions in the infrared, those of the latter being much more conspicuous (with a strong, broad absorption from 8.3–9.5 μ; a medium, strong line at 12 μ; two weaker lines at 12.82 μ and 14.38 μ). Either agent could be used on sodium chloride without resulting absorptions, but it was found undesirable to use titanium oxide on potassium bromide, because grains of the pol-

ishing agent were easily imbedded in its softer surface, with the result that the titanium oxide spectrum was superposed on that of the sample.

Cells used for volatile liquids and solutions were built after a modification of the design described by Randall.[33] Two NaCl (or KBr) plates, 4.3 × 3.0 × 0.8 cm, are channeled out to accommodate a mercury seal around the sample. The mercury seal is vacuum tight. Thus it becomes possible to place the cell inside the evacuated source box without losing the sample even though it be highly volatile. A platinum shim is used to define the liquid sample thickness. A set of shims varying in thickness from .005 mm to .30 mm was available.

Occasionally, a very hygroscopic compound needed to be prepared in a dry atmosphere. For this purpose, an air-tight box with suitable lighting, observation windows and hand openings was employed. In it, an operator, wearing rubber gloves, could perform all manipulations necessary in preparation of the sample for analysis without exposing the compound to undried air.

Paraffin Oil Paste Samples

The standard procedure for solid samples was to make a paste or suspension of the powdered sample in repurified commercial paraffin oil. The oil and the solid sample were ground together in a cone-shaped glass mortar, capacity about 1 cc, with a carefully fitted cone-shaped glass pestle. A 15 or 20 second grinding period was usually sufficient. After every 5 seconds of grinding, the paste, which had squeezed up out of the mortar onto the upper part of the pestle, was scraped back down onto its lower part for regrinding. The paste when ground sufficiently was placed, with the aid of a small spatula, along one edge of a salt plate. The salt cover plate was then slipped over it and squeezed down, spreading the paste layer evenly between the two plates.

Two preparations were made for running the full spectrum. For most compounds 10 mg of sample in 2 drops (25 mg) of paraffin oil was found most satisfactory in the 2–8 μ region and about 30 mg of sample in 2 drops of paraffin oil gave best results from 8–15 μ. If necessary, it is possible, by taking more time, to get a satisfactory spectrum from as little as 3 mg of sample, the amount of paraffin oil being reduced proportionately. The usual procedure gave an absorbing layer of sample containing about 1 mg per cm^2. This corresponds to a paste thickness of approximately .01 mm. It was found possible to prepare samples in an average time of less than fifteen minutes per sample.

There are many advantages to this well-known oil paste method of preparing solid samples for infrared spectrum analysis: applicability to almost all solid compounds; ease and speed of sample preparation; increased sharpness and definition of absorption bands because of the reduction of scattering from the solid layer; and uniformity of the solid layer thickness allowing standardization of operating conditions. The uniformity of concentration of the sample is nearly as good as that of solutions and the paraffin oil method has one decided advantage over solution work in that the oil itself is so transparent. The infrared spectrum of paraffin oil contains only 4 absorption lines between 2.5 μ and 15.5 μ, a strong doublet at 3.43 μ and 3.51 μ, and two medium-strong absorptions at 6.85 μ and 7.27 μ.

Solid Deposit Samples

When an unsatisfactory spectrum is obtained with the paraffin oil paste method, or when interest is focussed particularly in one of the regions partially masked by the paraffin oil absorption, solid samples may be laid down on an appropriate supporting plate by evaporation from any one of a wide variety of solvents. Solvents which were used in this work include:

acetic acid	formic acid
acetonitrile	heavy methanol
acetone	heavy water
acetophenone	methanol
aniline	methyl cellosolve
benzene	morpholine
benzyl alcohol	nitrobenzene
carbon tetrachloride	nitromethane
chloroform	N-methyl morpholine
cyclohexanone	piperidine
dioxane	pyridine
ethanol	tetrachlorethane
ethyl formate	water

The reason for such a large number of solvents was not merely that variety was needed to meet

[33] H. M. Randall, *Rev. Sci. Instr.* **10,** 195 (1939).

the initial problem of dissolving the solid samples. Certain samples were soluble in half a dozen or more solvents but when the solvent evaporated the solid deposit would in some cases be unsatisfactory as a solid layer for spectrum analysis, having crystallized into large crystals with transparent gaps between, or into fine powdery crystals which scattered radiation badly. Thus a variety of solvents had to be tried until one was found which gave a satisfactory solid layer, preferably a transparent, amorphous or glassy film or a layer of large uniform crystals. When no one solvent gave satisfactory layers, the expedient of mixing solvents was sometimes successful. Spectrograms have been made from solid deposits from the following mixed solvents: water and ethanol, pyridine and chloroform, pyridine and dioxane, pyridine and methyl cellosolve. When the proper solvent had been determined, it proved most satisfactory to place about 10 mg of the solid powder sample on a rock-salt plate, add a number of drops of the solvent directly to the solid, puddle the components of the resulting solution together on the plate with a small spatula and finally allow the solvent to evaporate leaving the solid layer on the supporting plate. When a compound had a low, stable melting point, it was sometimes more satisfactory to melt a few milligrams of it between salt plates, squeeze the resulting liquid between the plates and allow it to crystallize in a thin layer as it cooled.

Liquid Samples

Pure liquids were placed in the mercury-sealed NaCl or KBr cells already described. Film thickness ranged from very thin films (made by using the cell without any shim) to those made by shims from 0.005 mm up to 0.15 mm thick. Very heavy liquids and greases were satisfactorily placed between unchanneled salt plates which were squeezed together in a cell holder to make a thin film.

Solutions

All solutions were run in the mercury seal cells using shim thicknesses varying from 0.02 mm to 0.25 mm. Table 11 lists the solvents found useful during the work.

TABLE 11. SOLVENTS FOUND USEFUL IN SOLUTION SPECTRA

Solvent	Solvent Thickness, mm	Useful Spectral Region, μ
Acetone	0.04	12.0–18.8 19.2–24.
Carbon tetrachloride	.15	2.0– 6.2 6.7–12. 14. –15.5
Carbon tetrachloride	50.0	2.0– 4.2 4.5– 4.9 5.6– 6.0 7.1– 7.5
Chloroform	.04	2.8– 3.3 3.6– 6.3 6.3– 8.0 8.5–12. (if thin)
Dioxane	.04	3.8– 6.7
Ethanol	.04	3.8– 6.9 8.0– 9.0 10.0–11.2 11.7–13.
Heavy methanol	.04	4.2– 8.8 10. –15.
Heavy water	.02	4.3– 8.0 8.5–15.
Methanol	.04	3.8– 6.5 6.6– 8.8 10. –12.
Methyl cellosolve	.04	12.2–15.0
Pyridine	.02	3.7– 6.3
Water	.02	7.1–15.

There has been some question as to the relative merits of the spectra of compounds run in the solid state and in solution. The advantages of the former when prepared in paraffin oil paste form have already been mentioned. Solution samples also have advantages including uniform-

ity of layer thickness and ease of preparation. It is possible also by using non-polar solvents and low solute concentration to cut down bond association, sometimes prominent in molecular spectra. There are two disadvantages to solution spectra, the complexity of the solvent's own absorption and the limit to application imposed by solubility. The spectrum of the solvent used is superposed on the spectrum of the sample, and the more effective and universal solvents have the more complex and intense spectra. (That is, CCl_4 has a relatively weak spectrum up to a thickness of 0.15 mm, but its solvent properties are limited; on the other hand, pyridine, which is an effective solvent for a wide variety of compounds, has an intense and complicated spectrum of its own even in layers 0.02 mm thick.)

The optimum condition for analysis is met if both the solid and the solution spectrum of a compound can be obtained, for the study of the changes in wavelength and intensity of absorption bands when a sample goes from a crystalline state into solution is additional information often of real value in the analysis.

Chapter VII

SPECTRA OF VARIOUS COMPOUNDS

The infrared spectra of the compounds included in this book have been reproduced as halftones from the original records, and are reduced only a little more than 50 per cent. The wavelengths of what the authors and their several assistants have concluded to be actual major absorptions in each spectrum are marked upon the records themselves. It seemed advantageous to reproduce the original records rather than transfer the data to line charts, or trace off the envelope of the absorption as a graph. When these latter methods are employed, the reader is at a disadvantage in being compelled to rely wholly upon the opinion of the individual who made the tracing, concerning the reality of any particular absorption. Experience has shown that these methods err either by presenting too many absorptions, or too few. Many factors not immediately discernible influence the transcriber, among which wishful thinking is not the least, if the transcriber is also, in part, the interpreter of data, as he usually is. By presenting the original records it is felt that this factor for error is avoided, since he who does not subscribe to the given interpretations, has the records on hand permitting him to make his own deductions.

The grouping of structural configurations indicated in Chapter I is adopted in this catalogue as a convenient method of arranging the spectra. Each spectrum is numbered according to its sequence in the catalogue. Thus, first in order are placed fourteen acids, selected for this position because the carboxyl carbonyl group gives rise to the most distinctive absorption in their spectra. Next come twenty-two esters, grouped together because the ester carbonyl is their most distinctive absorption. This is then continued through salts, amides, etc., as outlined in Chapter I. Since many compounds have more than one distinctively absorbing group, and since any one record is reported in only one place, i.e., under the group which has been arbitrarily regarded as the most distinctive, it is necessary to have a cross-index of the spectra of all compounds having a given absorption. This is done in Table 12, just preceding the catalogue. The plate numbers of all other compounds having absorptions related to the group under consideration are listed following the particular compounds of the group.

Each halftone is named and numbered. It carries in addition full information concerning the sample used in obtaining the spectrum. The methods of preparing and obtaining the requisite thicknesses of samples have been fully described in Chapter VI. As indicated there, solid samples were obtained in three ways: (1) by grinding in oil, (2) by fusion, (3) by depositing from solution. The words "oil," "fusion," or "deposited from *alcohol*" will describe the preparation of solid samples. The thicknesses of the solid samples are indeterminate, but are of the order of .01 mm. Thicknesses of all liquid samples are given in millimeters. Where the thickness alone is reported, a pure liquid is indicated. For solution spectra, a concentration and solvent are also given.

In studying these spectra it should be borne in mind that certain absorptions are not caused by the sample. Use of a vacuum instrument eliminates interference from water vapor and carbon dioxide, but the oil suspensions, and any solutions, contain bands arising from the oil or solvent. The paraffin oil lines are four in number, consisting of a narrow doublet at 3.43 and 3.51 μ, and single lines at 6.85 and 7.25 μ. These are strong, have their origin in the CH stretching and bend-

ing vibrations of the paraffin chains, and are usually marked "oil" in the halftones. In the examination of solution spectra, comparison should be made between the spectra of the solution and solvent to eliminate the lines of the latter.

Owing to what appears to have been a thin film of unknown nature deposited on the optical surfaces of the instrument as a result of an accident during its operation, there are three weak absorptions in these records which have no significance at any time since they were always present, even when no sample was placed in the beam. Of these, the one at 2.78 μ is usually evident, and is never measured. The others form a doublet with maximum absorptions at 7.22 and 7.38 μ. These lines have to be taken into account when interpreting the spectra at these points. The spurious absorptions usually are seen as sidehills on stronger bands, unless the whole spectrum is weak, when they are likely to appear prominent by contrast. The correctness of the explanation of the source of these bands was seen after the instrument was taken apart and cleaned, shortly following the making of these records. After the cleaning, the spurious absorptions disappeared completely.

TABLE 12. LIST OF SPECTRA

TABLE 12. LIST OF SPECTRA—*Continued*

TABLE 12. LIST OF SPECTRA—*Continued*

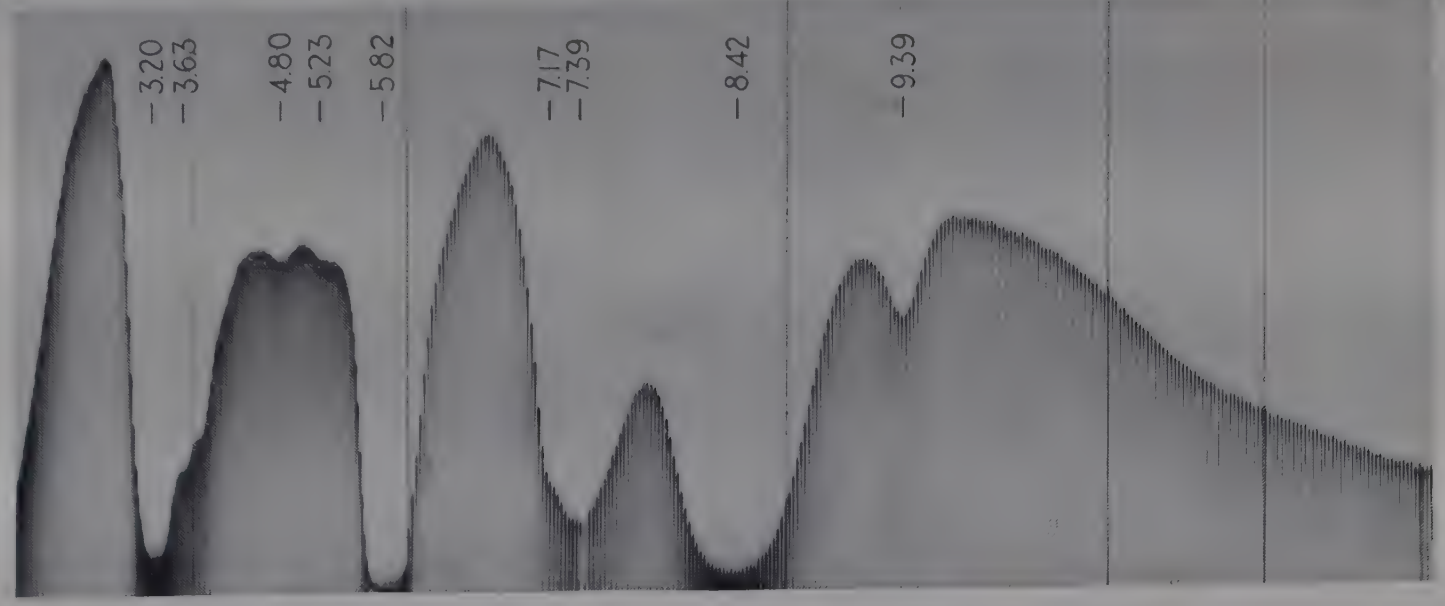
* This compound could also be grouped with the urethanes.

TABLE 12. LIST OF SPECTRA—*Continued*

TABLE 12. LIST OF SPECTRA—*Continued*

TABLE 12. LIST OF SPECTRA—*Continued*

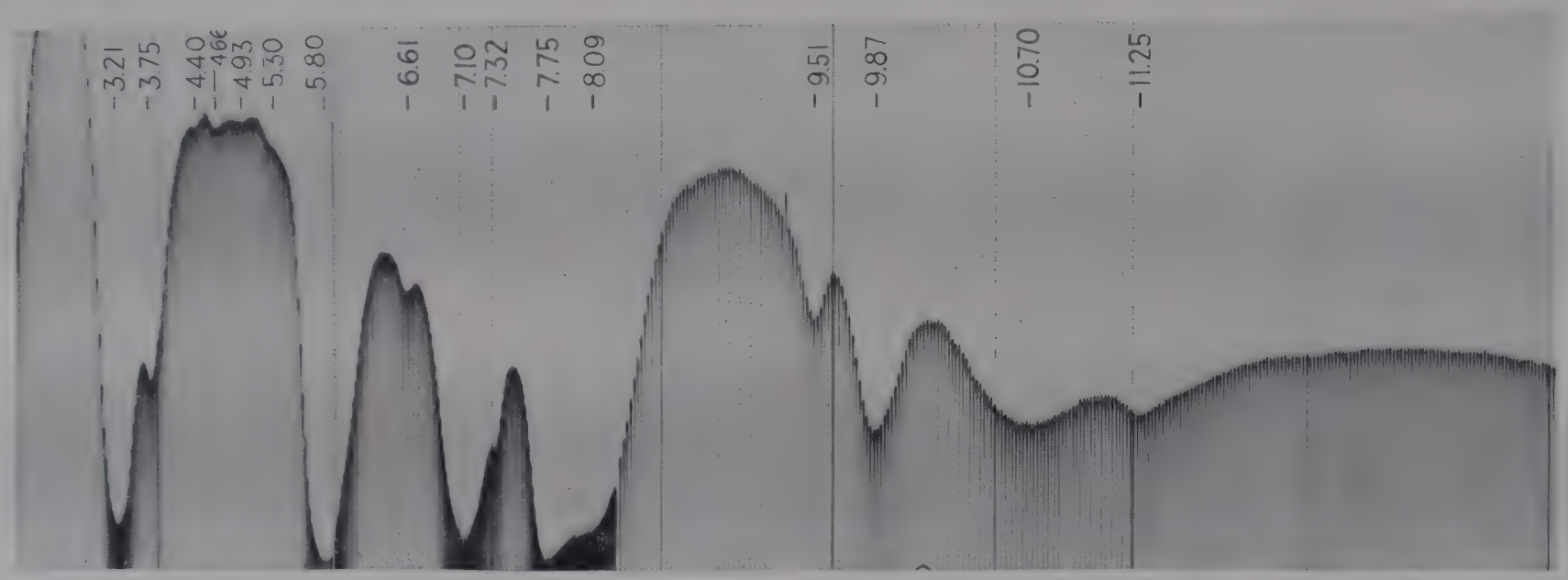
TABLE 12. LIST OF SPECTRA—*Continued*



FORMIC ACID

HCO_2H

PLATE 1. Assignments: 5.82 μ Acid C=O Preparation: 0.005 mm.

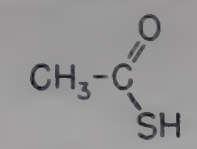


ACETIC ACID

$CH_3\text{-}CO_2H$

(Left)

THIOACETIC ACID



(Bottom)

PLATE 2. Assignments: 5.80 μ Acid C=O Preparation: 0.005 mm.

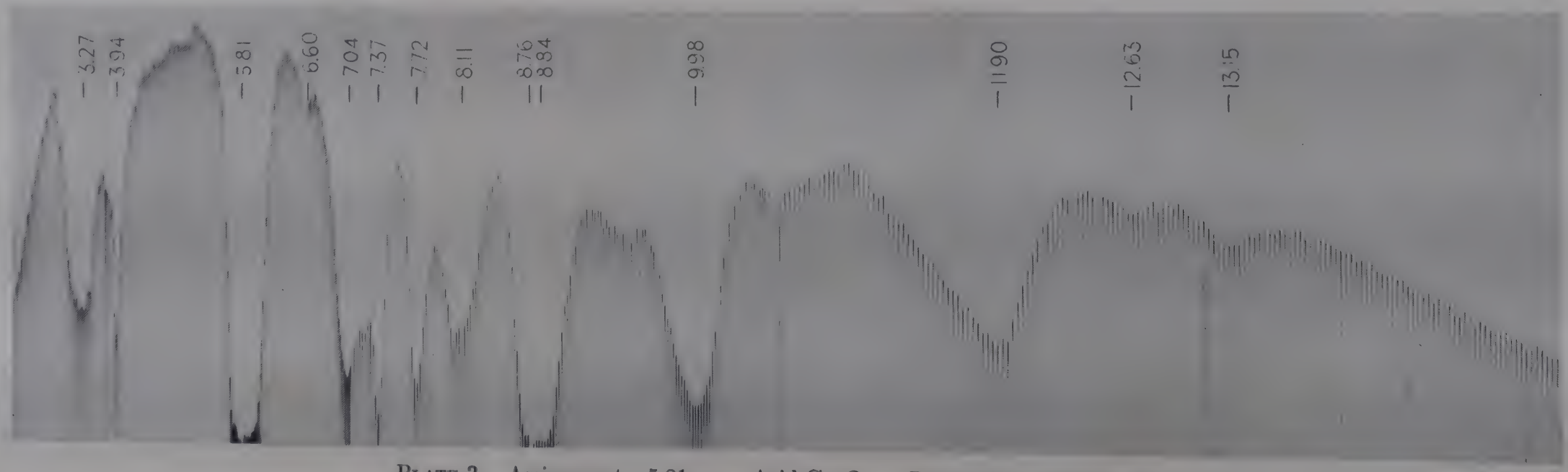


PLATE 3. Assignments: 5.81 μ Acid C=O Preparation: 0.015 mm.

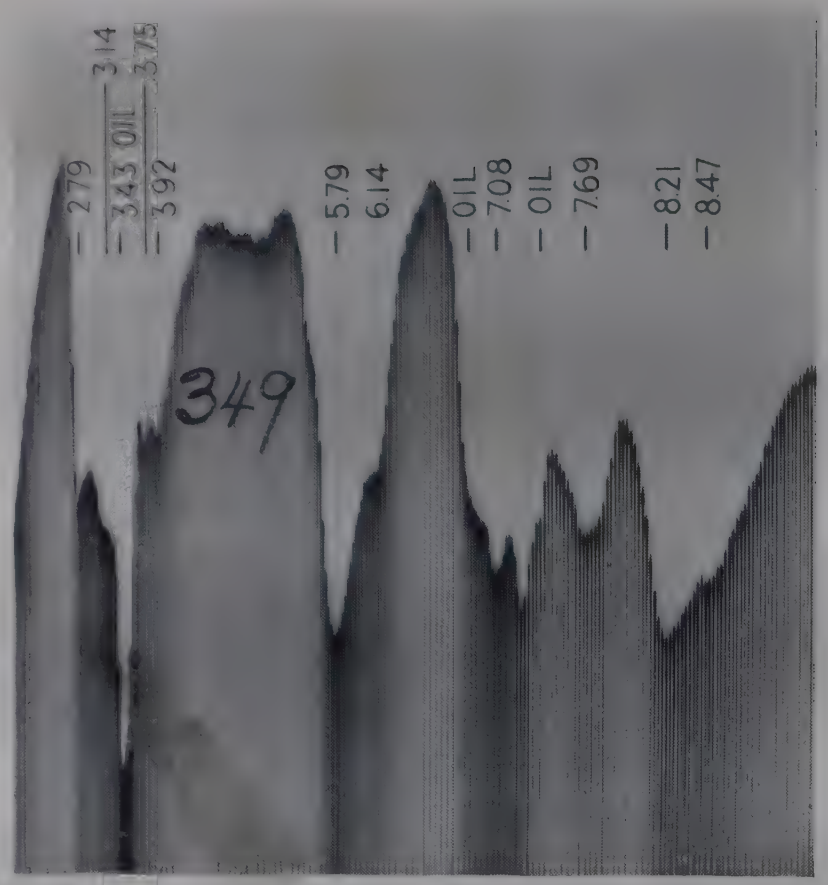


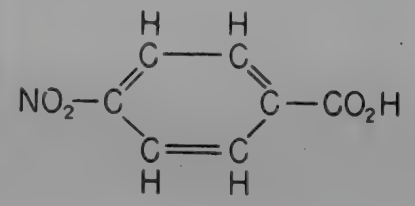
PLATE 4. Assignments: 5.79 μ Acid C=O
Preparation: Oil paste

CHLORACETIC ACID

$Cl-CH_2-CO_2H$

(Top Left)

p-NITROBENZOIC ACID



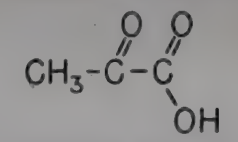
(Bottom Left)

BENZOIC ACID

$C_6H_5-CO_2H$

(Top Right)

PYRUVIC ACID



(Bottom Center)

GLUTARIC ACID

$HO_2C-(CH_2)_3-CO_2H$

(Bottom Right)

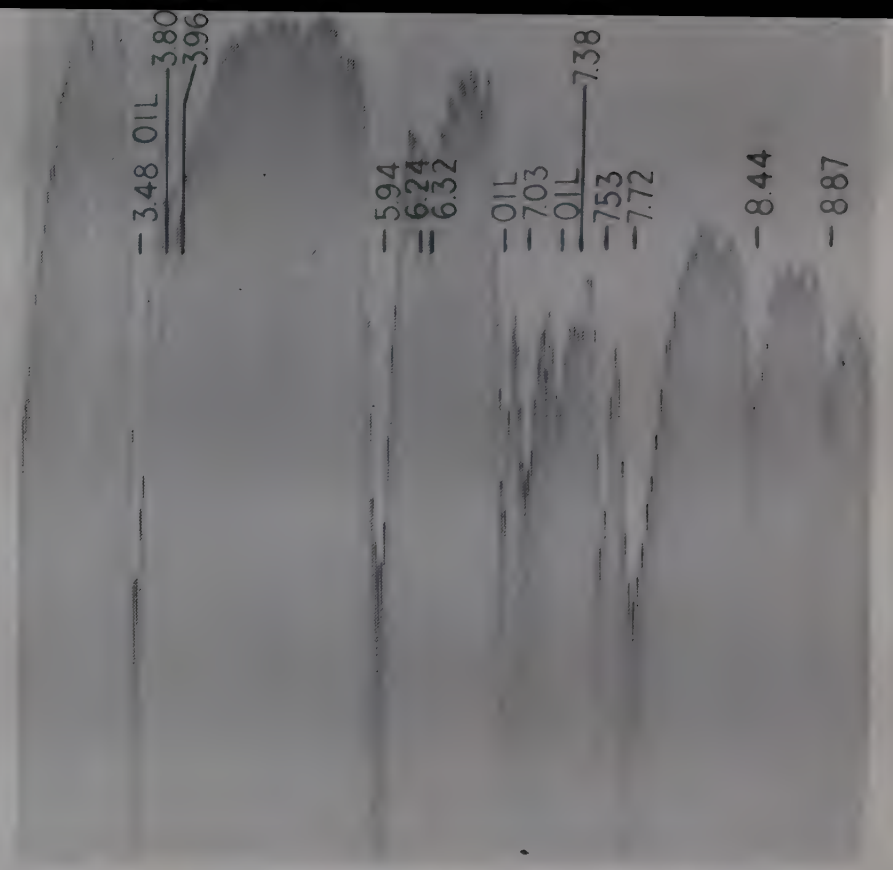


PLATE 5. Assignments: 5.94 μ Conjugated acid C=O
6.24 μ, 6.32 μ Conjugated benzene ring
Preparation: Oil paste

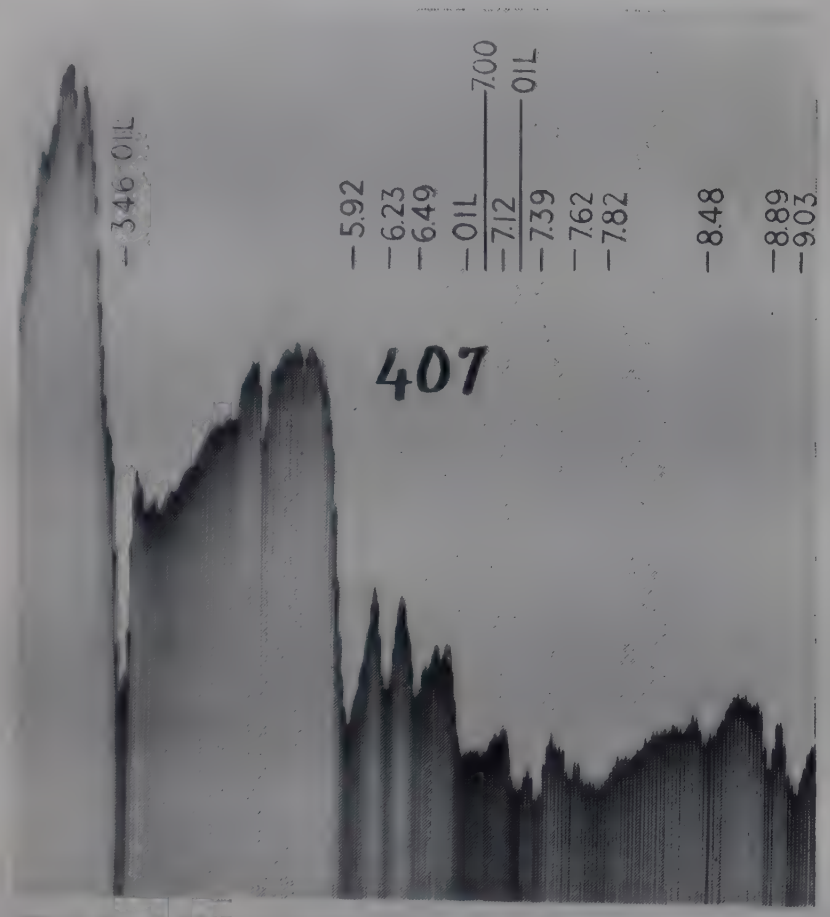


Plate 6. 5.92 μ Conj. acid C=O; 6.49 μ NO_2;
oil paste 6.23 μ, 6.70 μ Phenyl

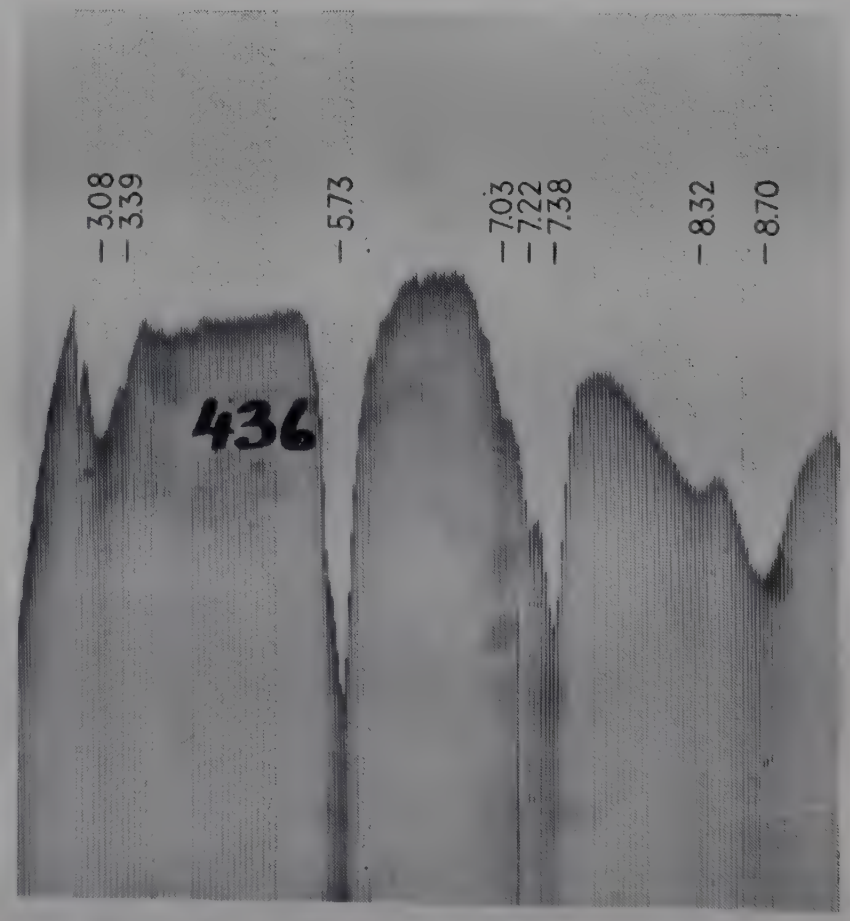


PLATE 7. Assignments: 5.73 μ Acid C=O
Preparation: Capillary cell

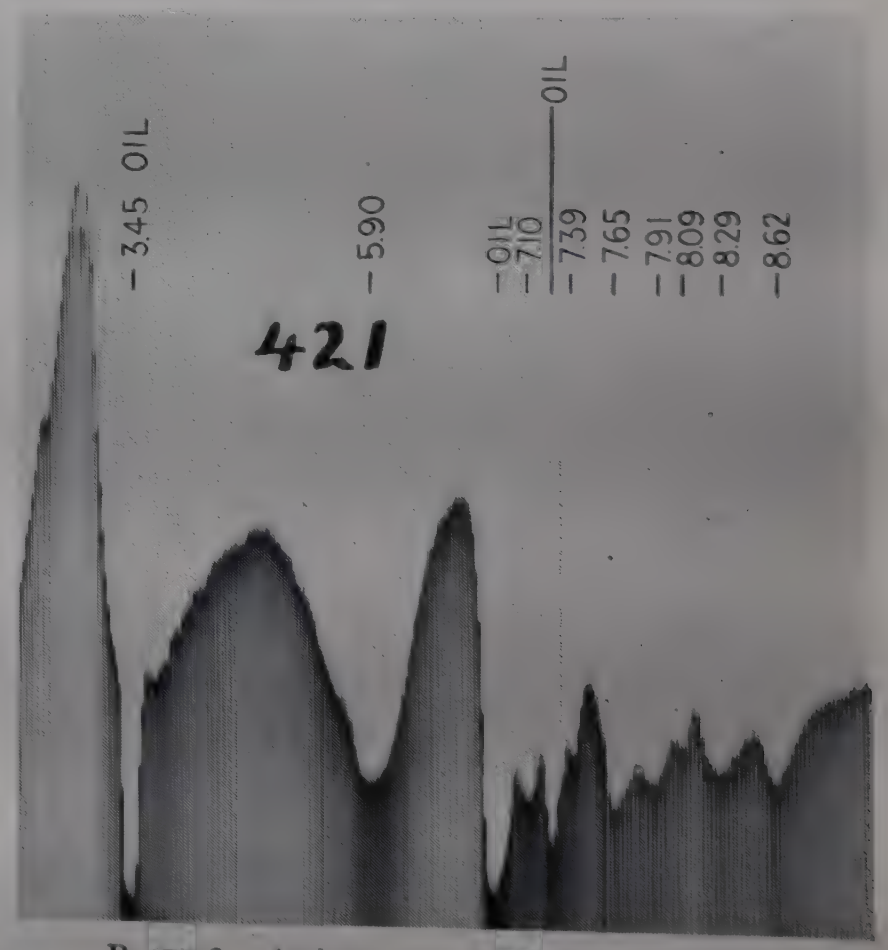


PLATE 8. Assignments: 5.90 μ Acid C=O
Preparation: Oil paste

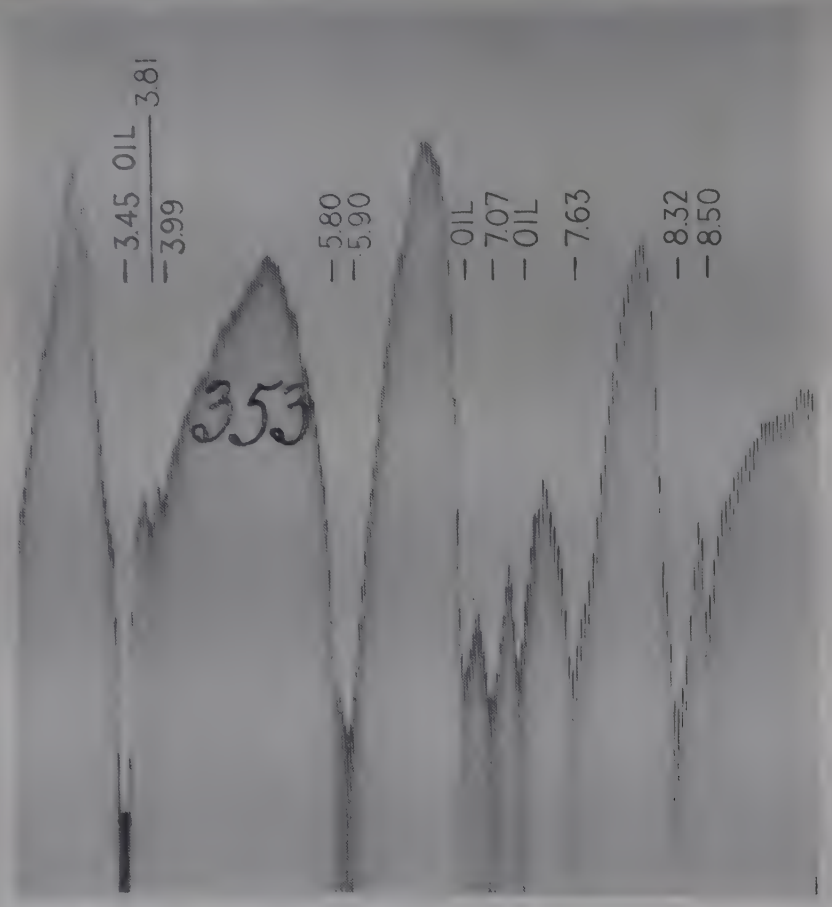
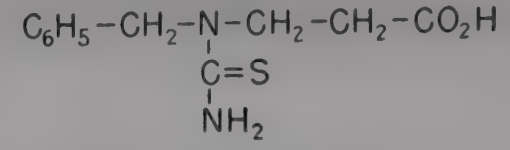


PLATE 9. Assignments: 5.80 μ, 5.90 μ } Acid C=O
Preparation: Oil paste

N-THIOCARBAMYL-β-BENZYLAMINOPROPIONIC ACID



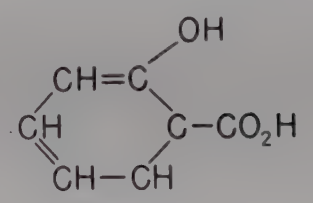
(Top Right)

SUCCINIC ACID

$HO_2C-CH_2-CH_2-CO_2H$

(Top Left)

SALICYLIC ACID



(Bottom Center)

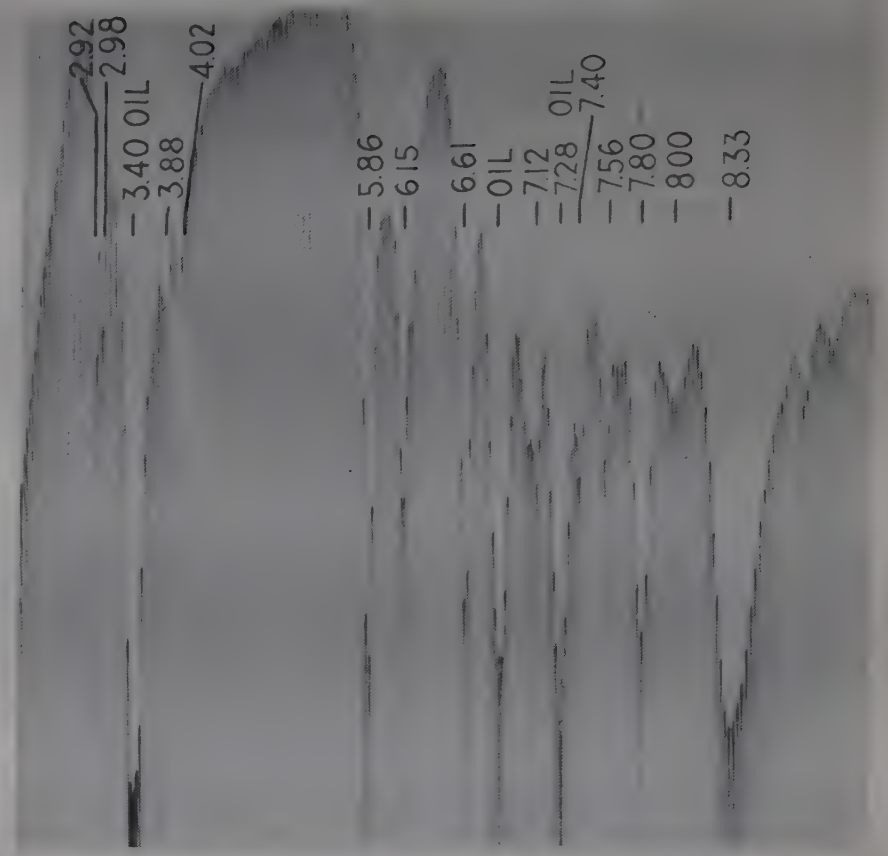


PLATE 10. Assignments: 5.86 μ Acid C=O
6.15 μ NH_2
6.61 μ Thioureide ion
Preparation: Oil paste

OXALIC ACID

HO_2C-CO_2H

(Bottom Left)

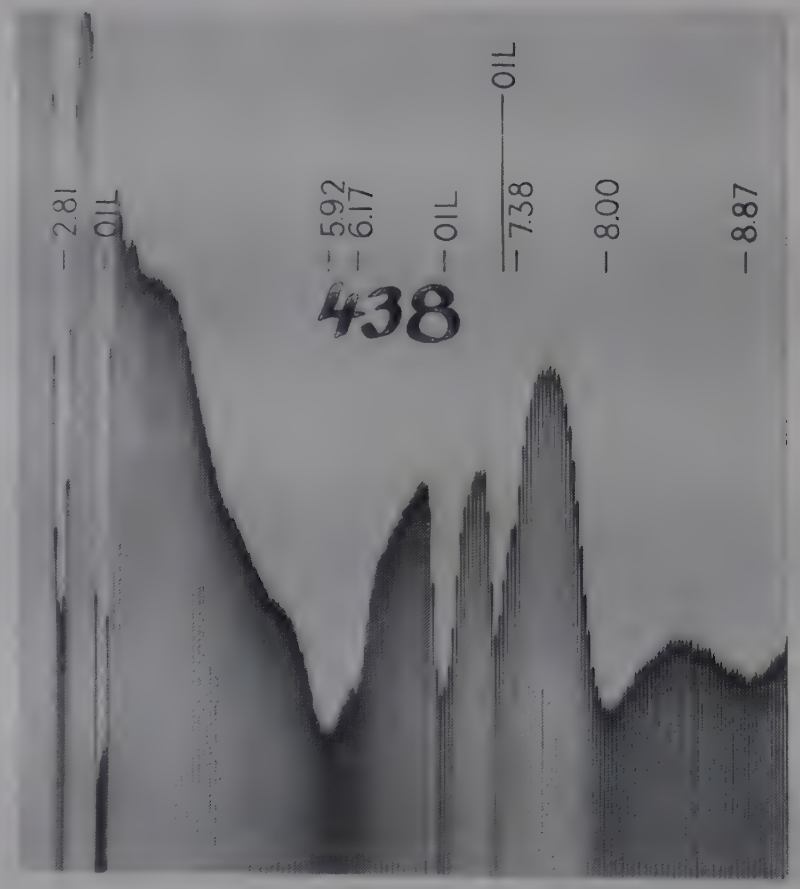


PLATE 11. Preparation: Oil paste

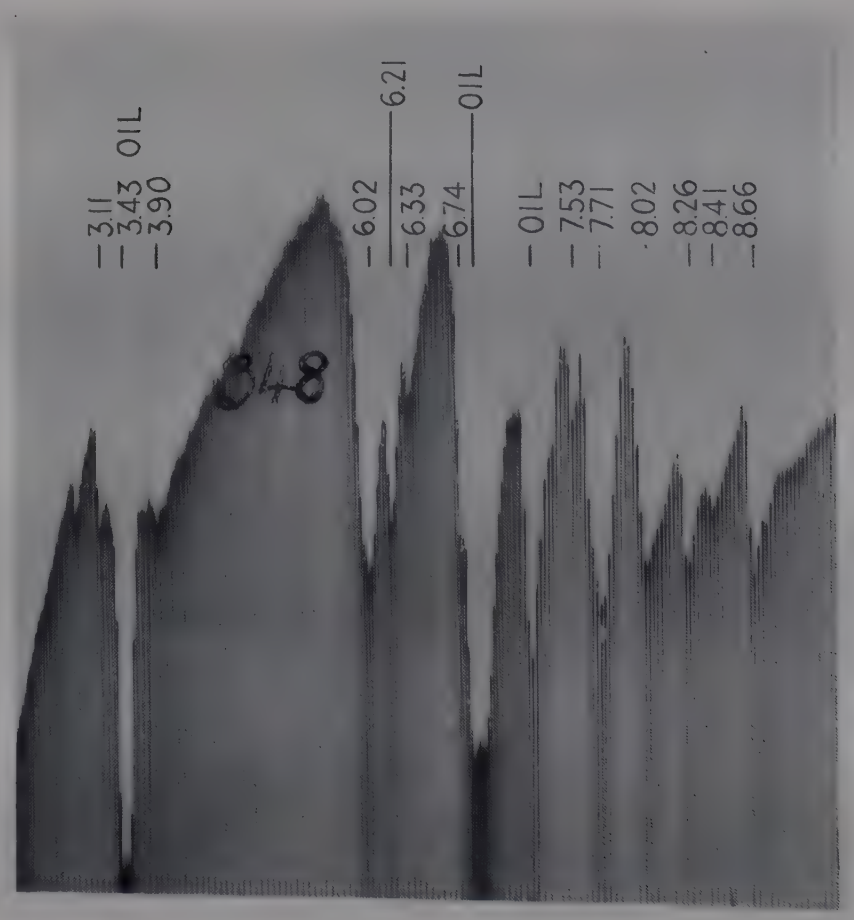
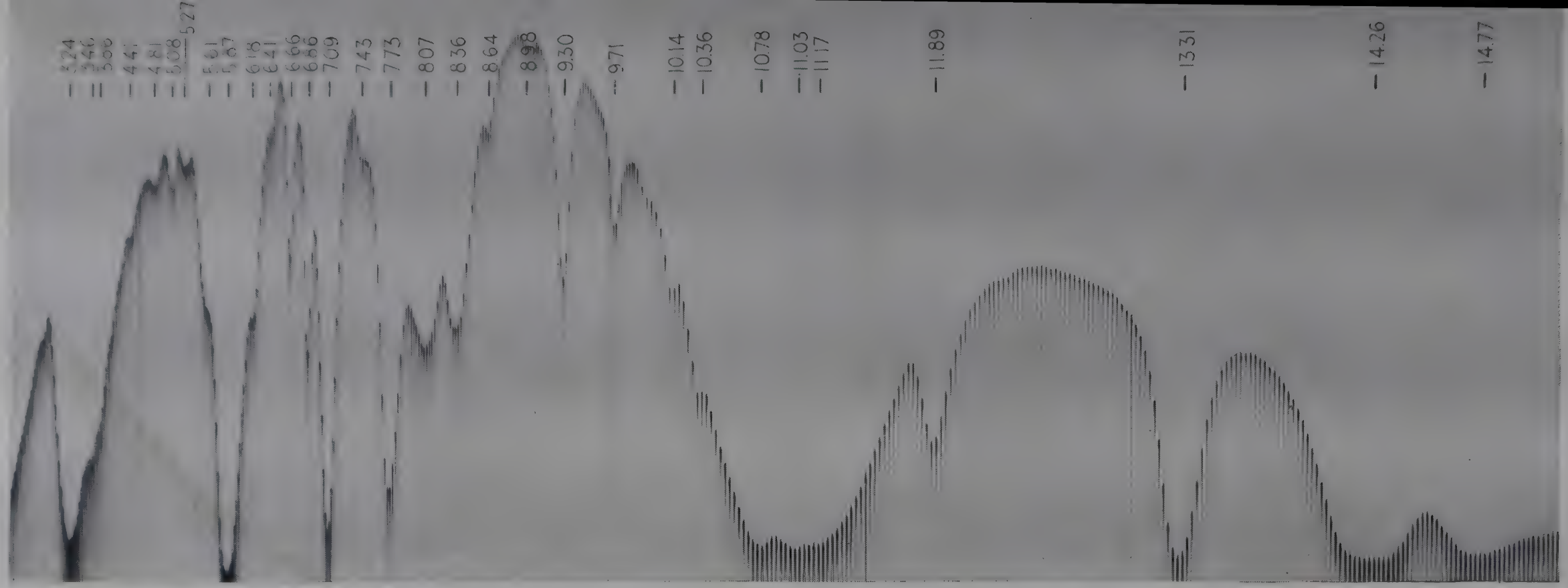


PLATE 12. Assignments: 6.02 μ Conjugated acid C=O
6.21 μ, 6.33 μ, 6.74 μ Conjugated *o*-Hydroxyphenyl
Preparation: Oil paste



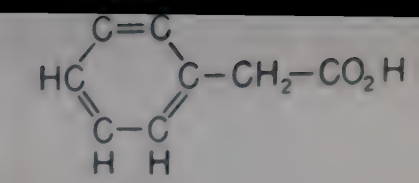
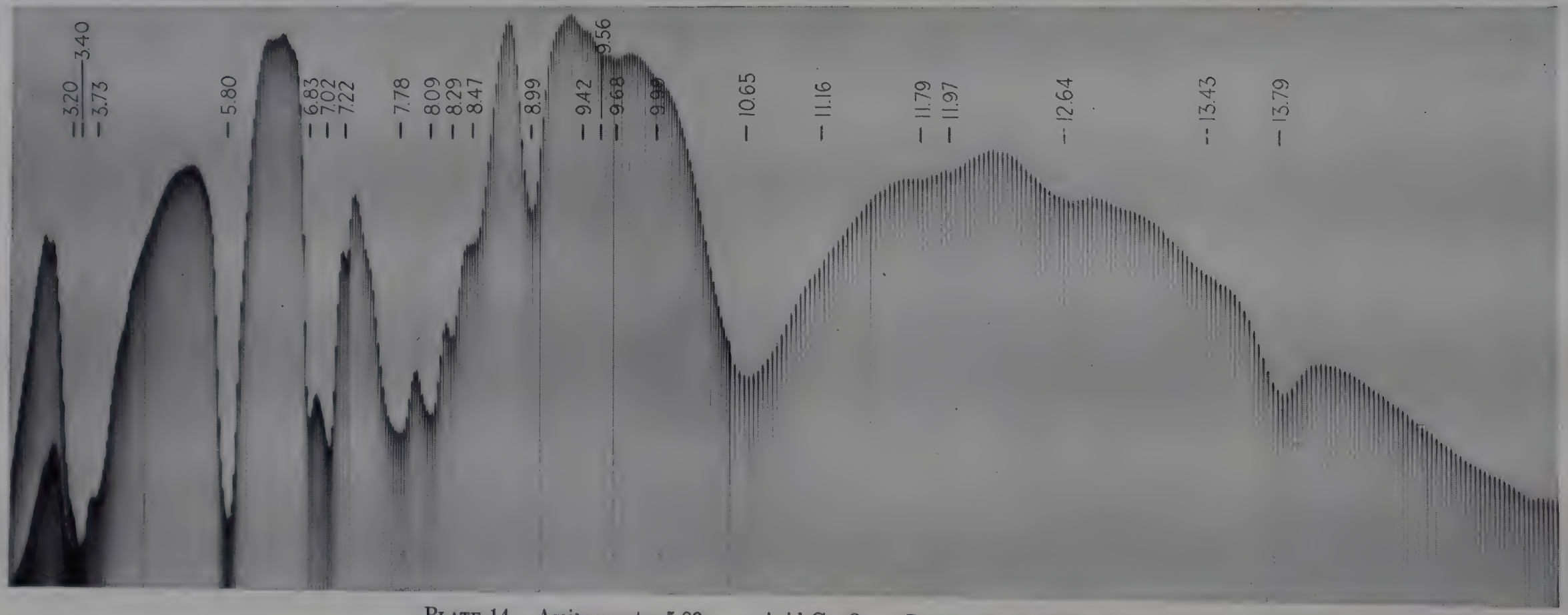


PLATE 13. Assignments: 5.87 μ Acid C=O 6.18 μ, 6.66 μ Phenyl Preparation: Melted and resolidified



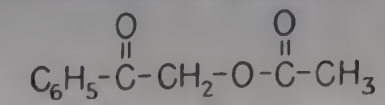
CAPRYLIC ACID

$CH_3 \cdot (CH_2)_6 \cdot CO_2H$

PLATE 14. Assignments: 5.80 μ Acid C=O Preparation: 0.02 mm.

ANTHRANILIC ACID METHYL ESTER
(*Top Left*)

PHENACYL ACETATE



(*Top Right*)

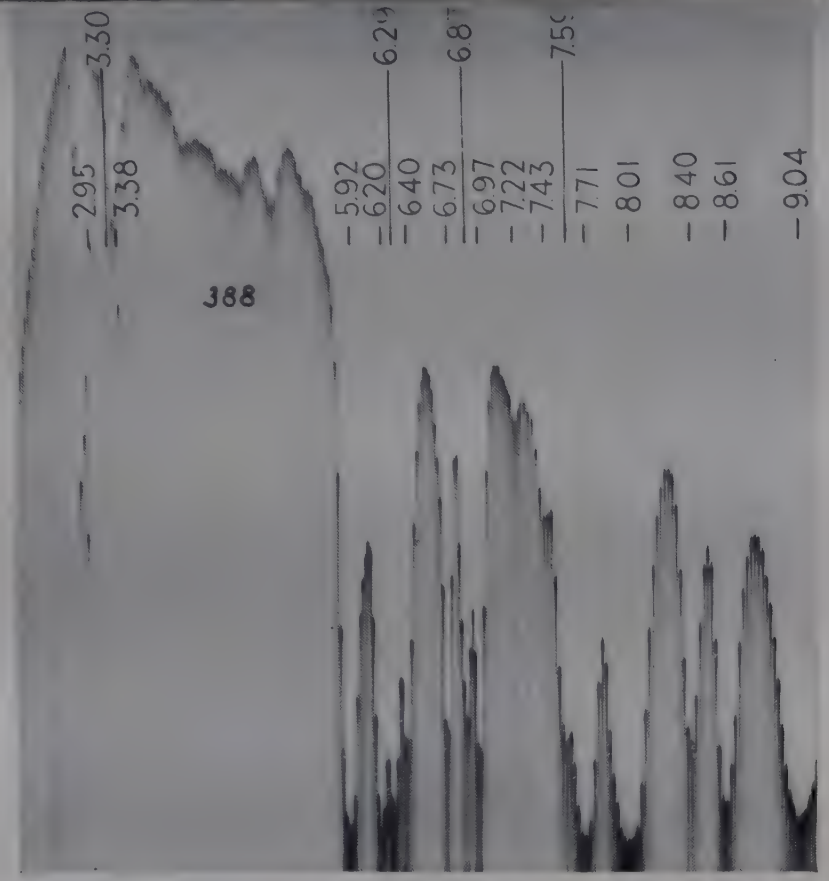
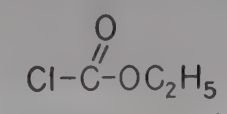


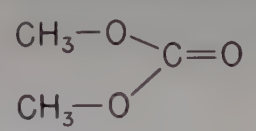
PLATE 15. 5.92 μ Conj. ester; 6.20 μ δNH_2, Phenyl; 6.29 μ Conj. phenyl; 6.40 μ Anilino; 6.73 μ Phenyl. Cap. cell

ETHYL CHLOROCARBONATE



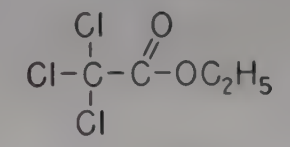
(*Bottom Center*)

METHYL CARBONATE



(*Bottom Left*)

ETHYL TRICHLOROACETATE



(*Bottom Right*)

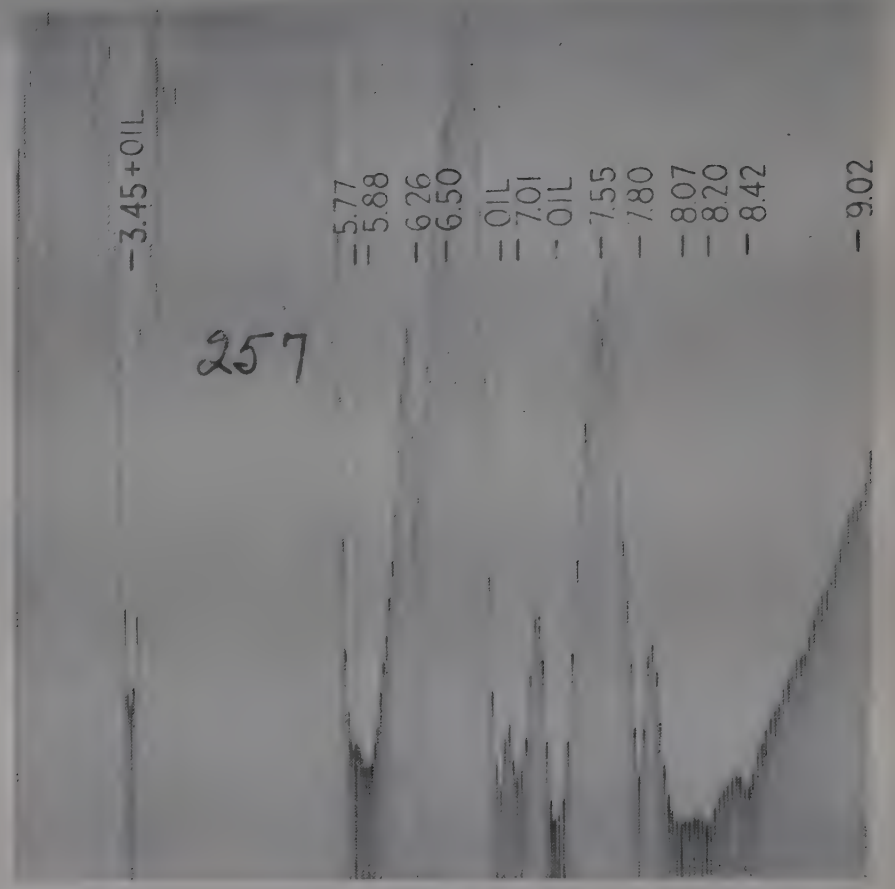


PLATE 16. Assignments: 5.77 μ Ester C=O; 5.88 μ Keto C=O; 6.26 μ Phenyl. Oil paste

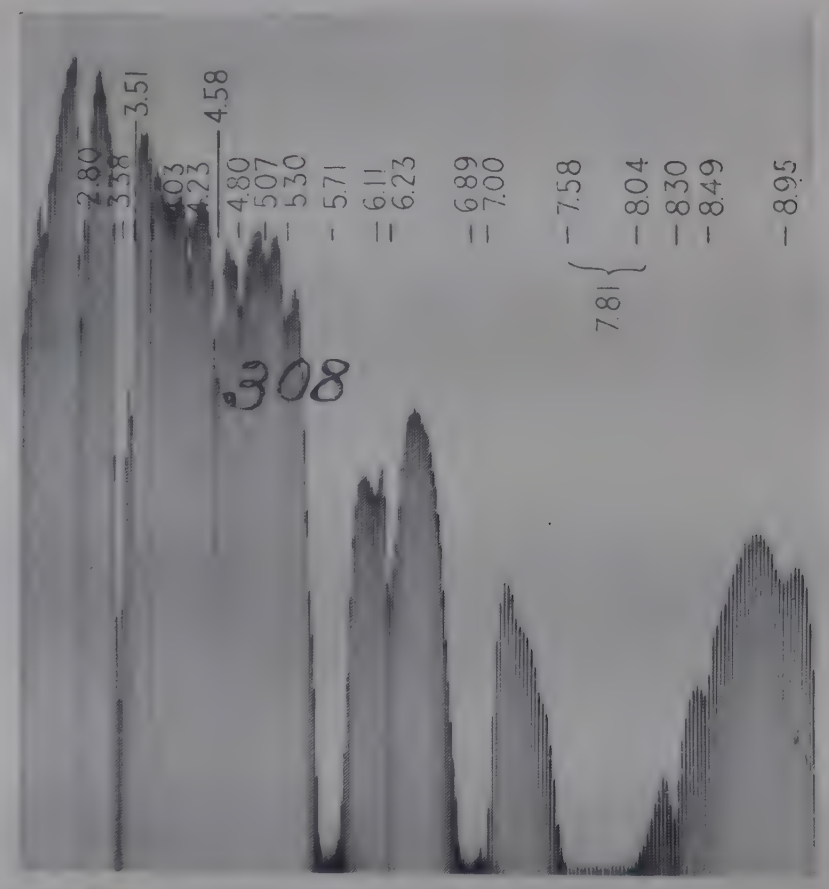


PLATE 17. Assignments: 5.71 μ Ester C=O
Preparation: 0.02 mm.

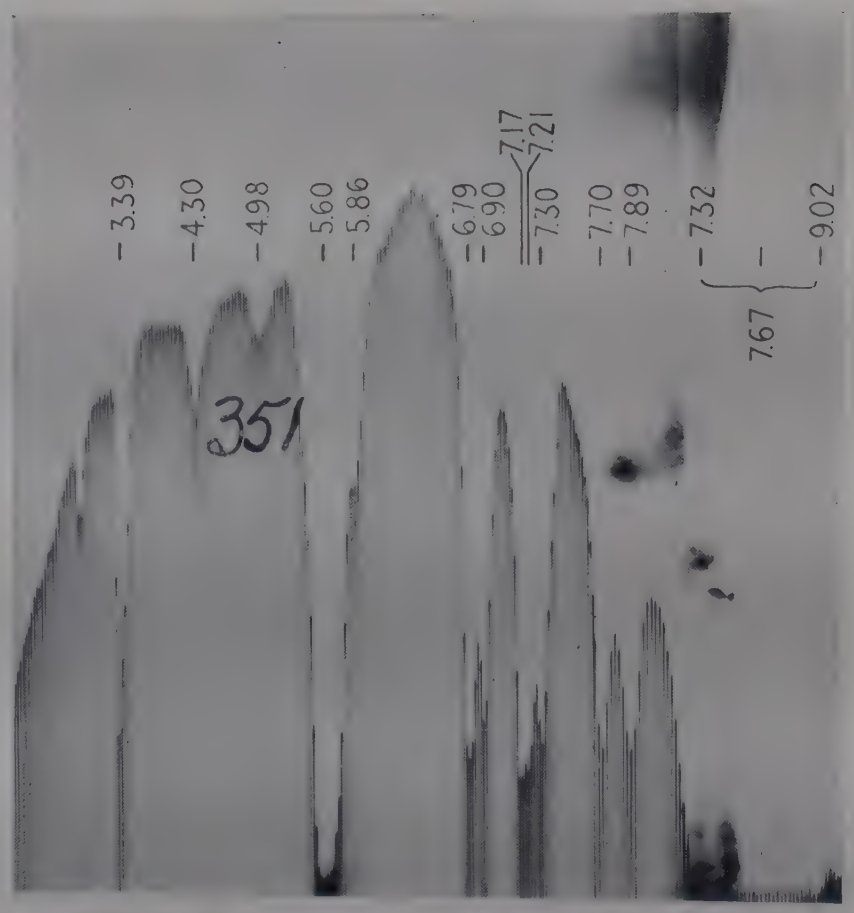


PLATE 18. Assignments: 5.60 μ Ester C=O
Preparation: 0.02 mm.

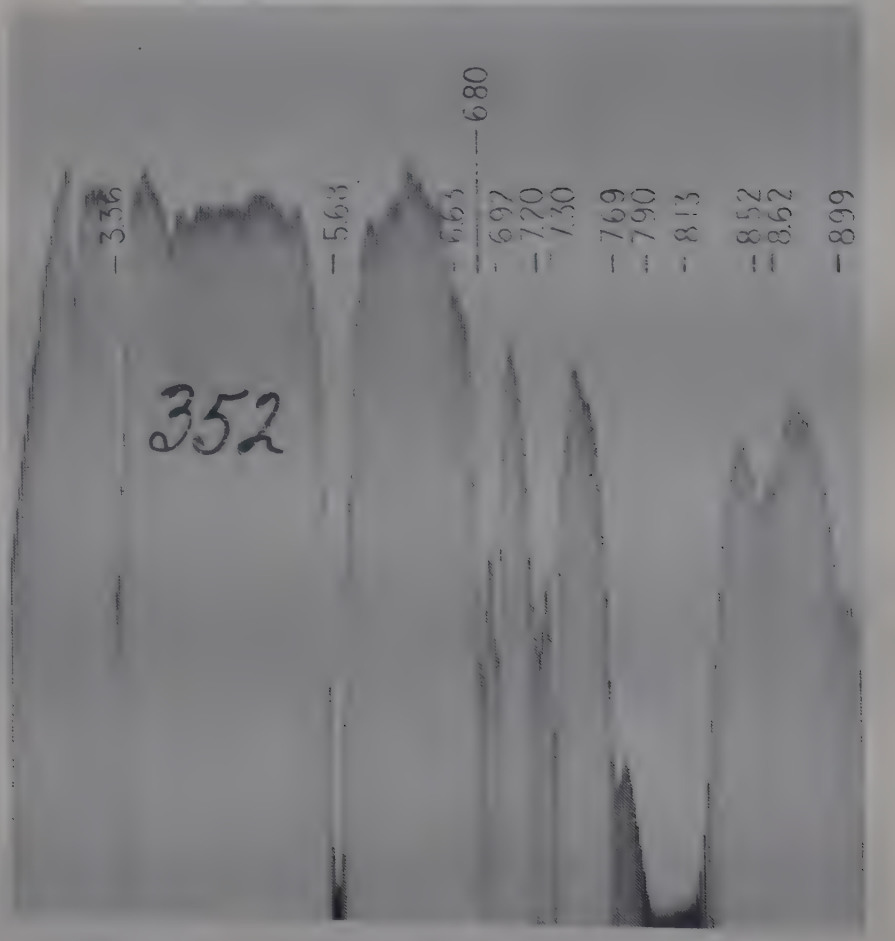


PLATE 19. Assignments: 5.68 μ Ester C=O
Preparation: Capillary cell

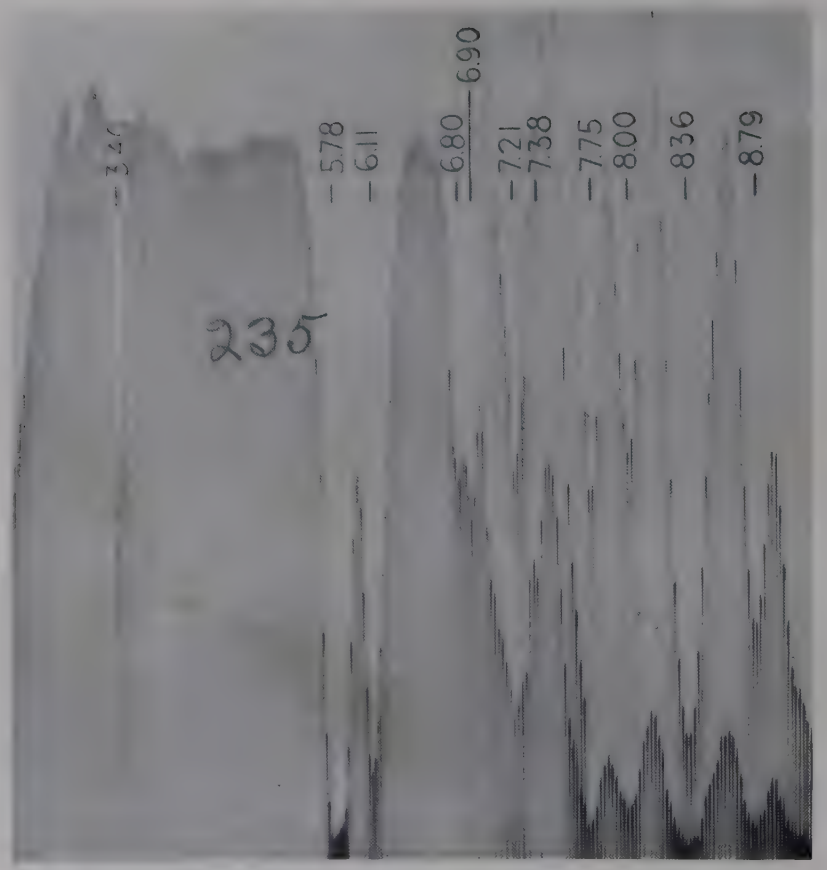
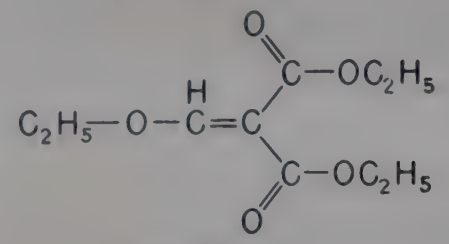


PLATE 20. Assignments: 5.78 μ Ester C=O (conjugated)
6.11 μ Conjugated C=C
Preparation: 0.02 mm.

ETHOXYMETHYLENE MALONIC ACID
DIETHYL ESTER



(Top Left)

N-PHENYLGLYCINE ETHYL ESTER
(Top Right)

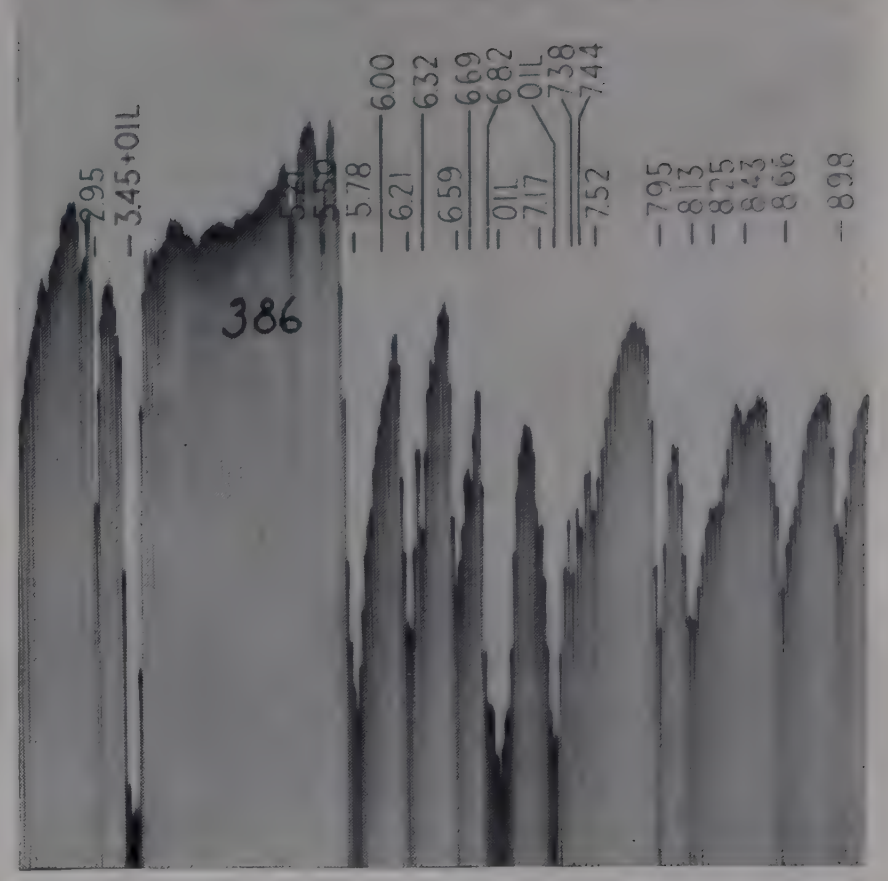
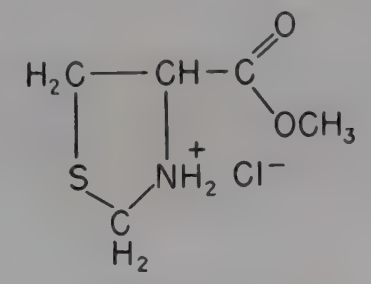


PLATE 21. Assignments: 5.78 μ Ester C=O
6.21 μ, 6.32 μ, 6.59 μ Phenyl
Preparation: Oil paste

THIAZOLIDINE-4-CARBOXYLIC ACID
METHYL ESTER HYDROCHLORIDE



(Bottom Center)

DEUTERO-N-PHENYLGLYCINE ETHYL ESTER
(Bottom Left)

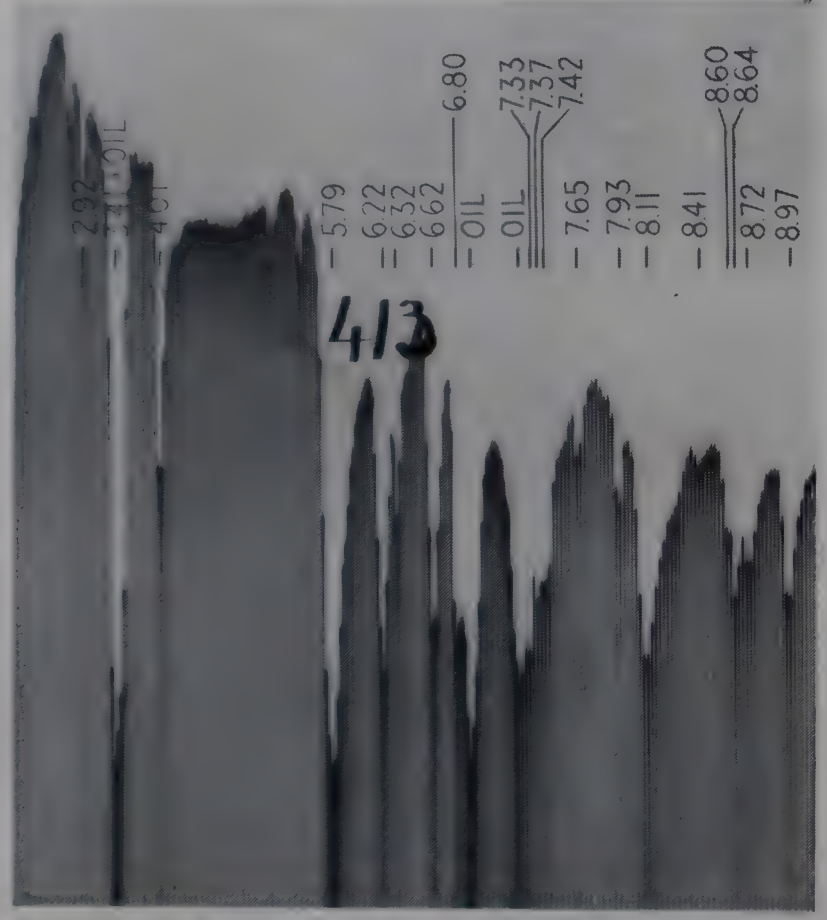


PLATE 22. 5.79 μ Ester C=O;
Oil paste

2-BENZYL-Δ^2-THIAZOLINE-4-
CARBOXYLIC ACID METHYL ESTER
(Bottom Right)

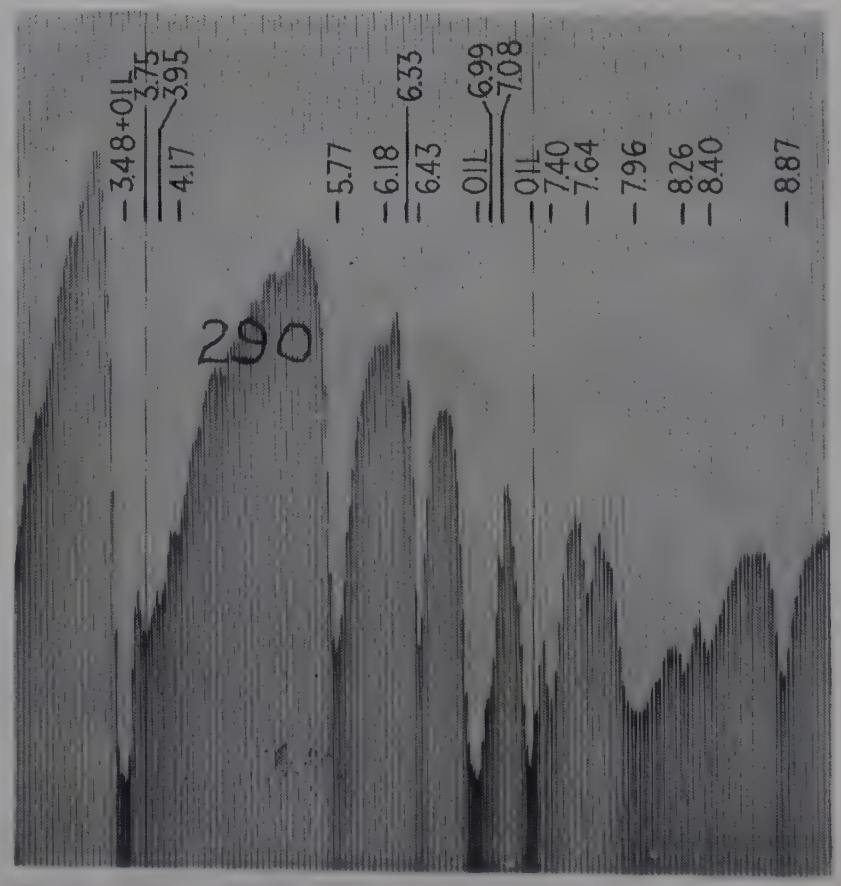


PLATE 23. 5.77 μ Ester C=O; 6.43 μ Unassigned.
Oil paste

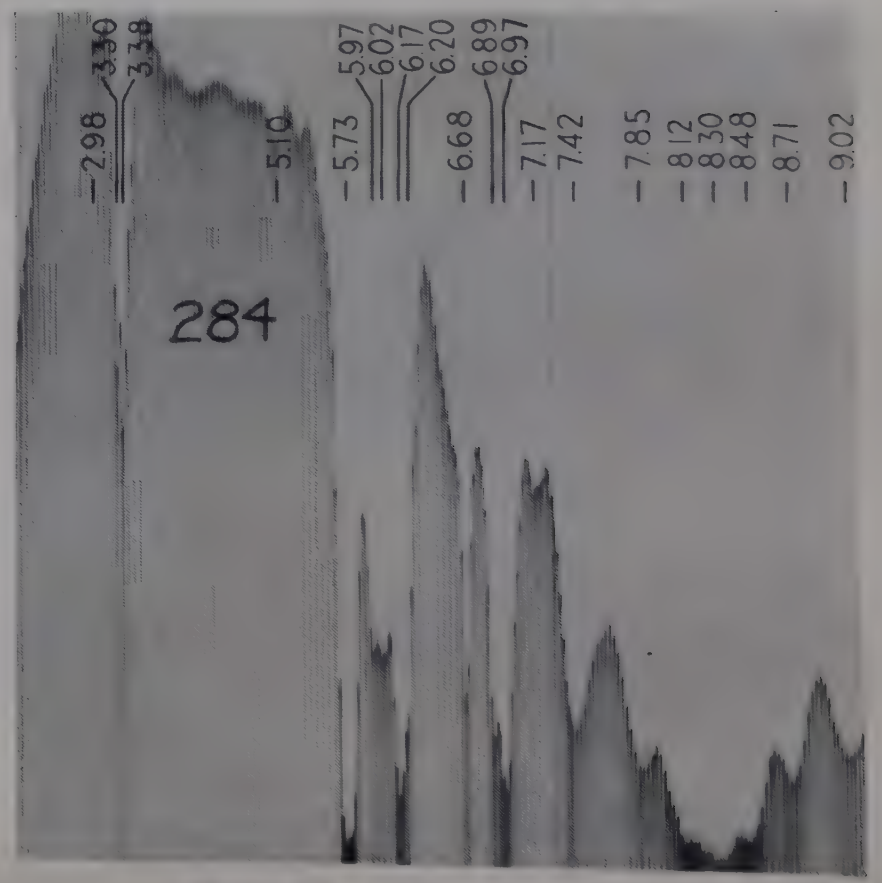


PLATE 25. 5.73 μ Ester C=O;
Oil paste

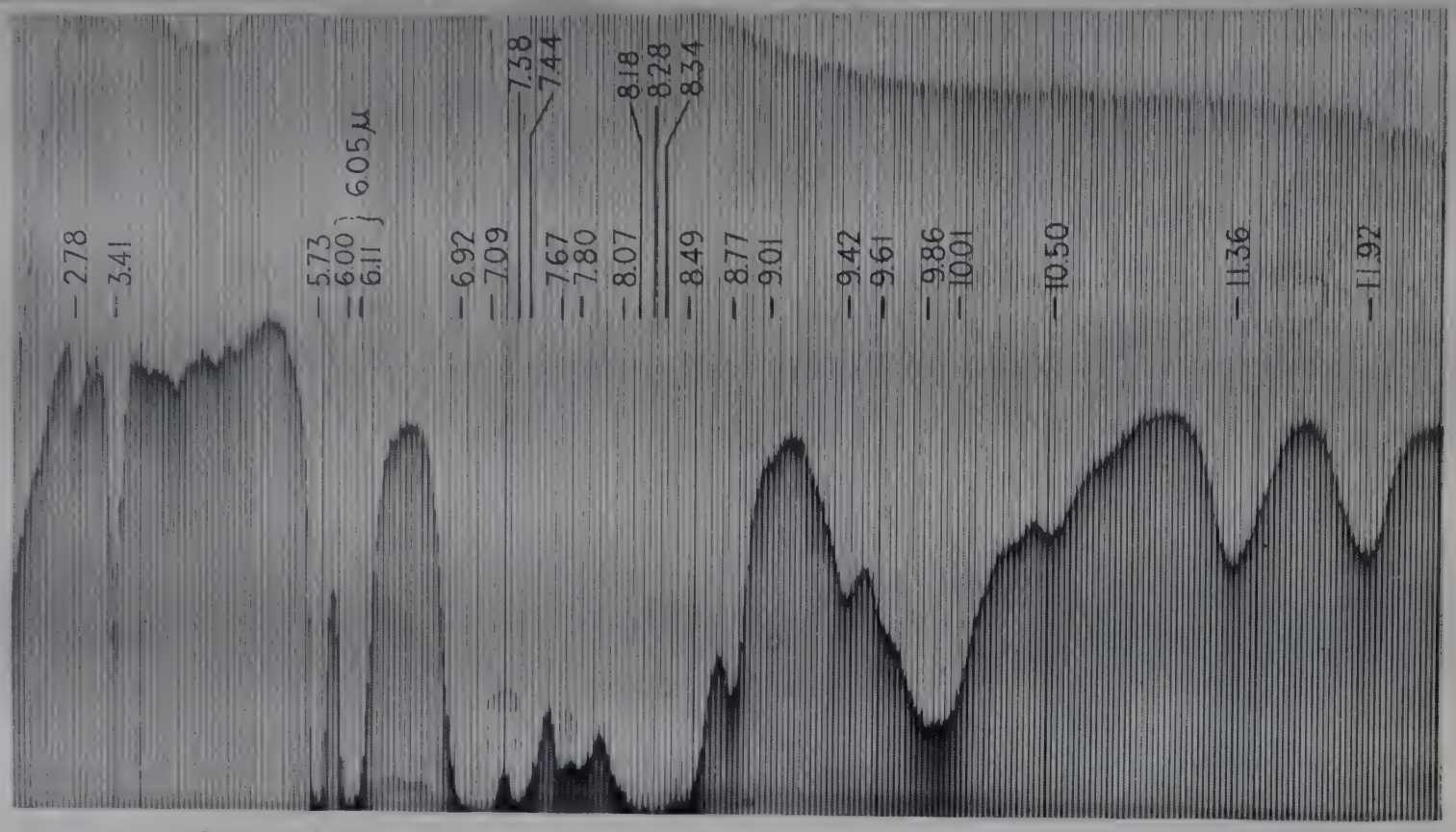
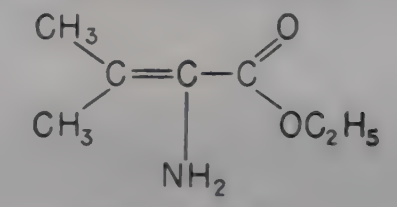


PLATE 24. Assignments: 5.73 μ Ester C=O
6.05 μ N-acyl C=O
Preparation: 0.015 mm.

N-ACETYLTHIAZOLIDINE-4-CARBOXYLIC ACID METHYL ESTER

(Top and Bottom Left)

α-AMINO-β,β-DIMETHYL ACRYLIC ACID ETHYL ESTER



(Bottom Right)

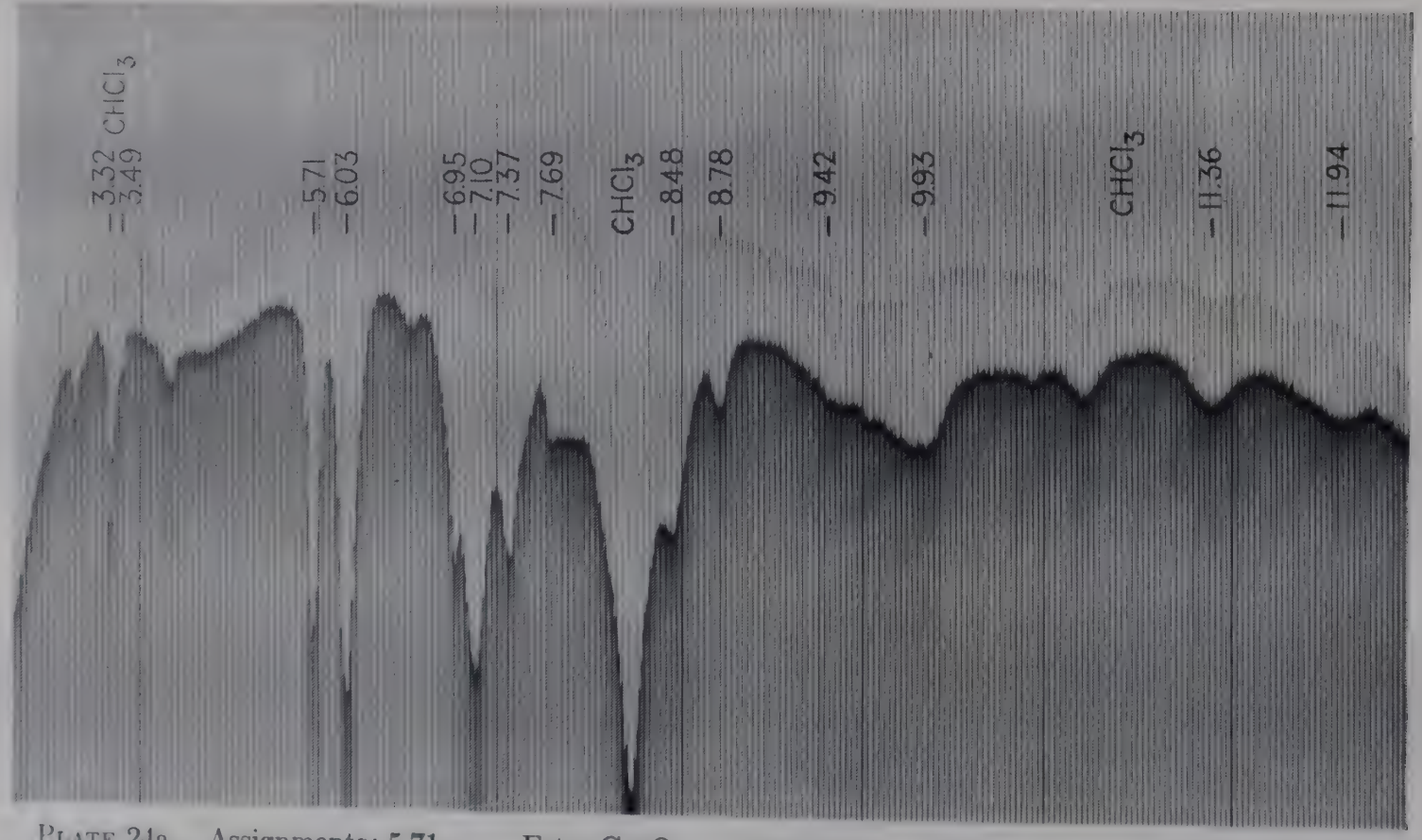


PLATE 24a. Assignments: 5.71 μ Ester C=O
6.03 μ N-acyl C=O
Preparation: 10% solution in $CHCl_3$, 0.015 mm.

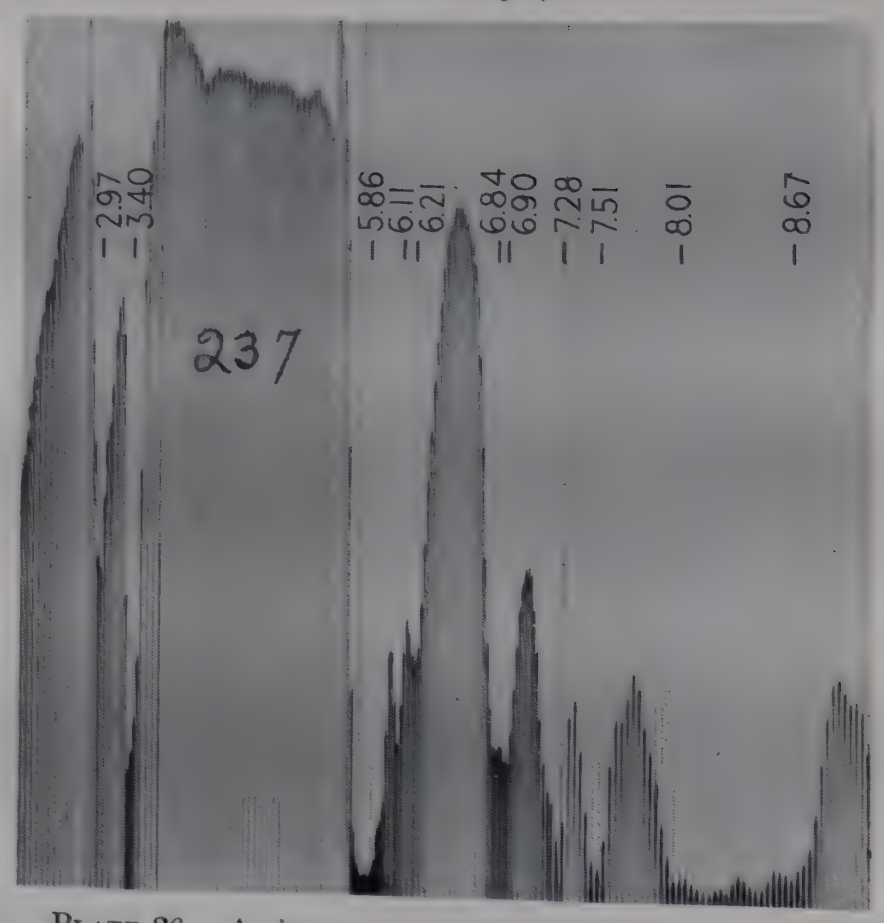


PLATE 26. Assignments: 5.86 μ Conjugated ester C=O
6.11 μ C=C conjugated
6.21 μ NH_2
Preparation: 0.02 mm.

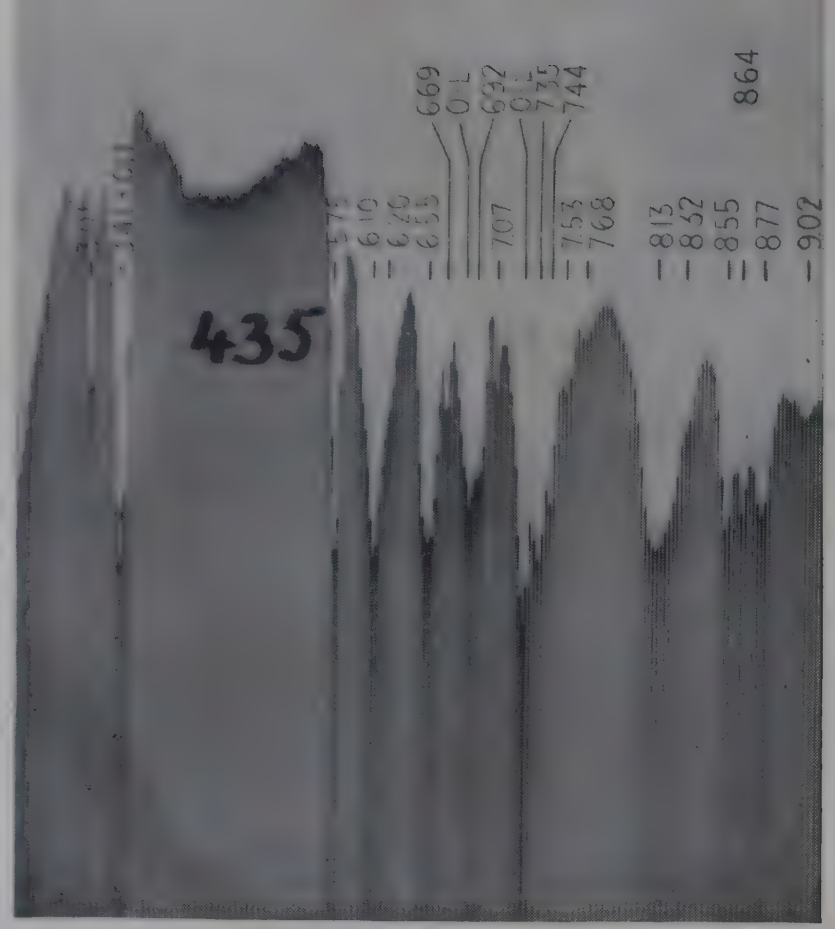
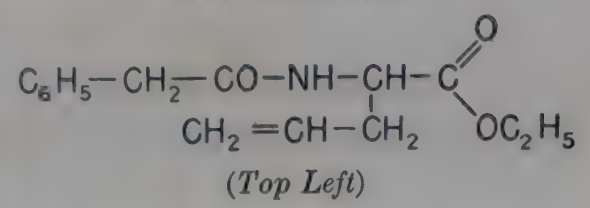


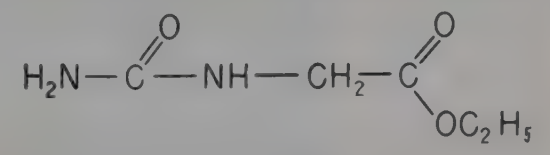
PLATE 27. 5.75 μ Ester C=O; 6.10 μ Amide I; 6.20 μ C=C, phenyl. Oil paste: 6.55 μ Amide II; 6.69 μ Phenyl.

α-ALLYLPHENACETURIC ACID
ETHYL ESTER



(*Top Left*)

HYDANTOIC ACID ETHYL ESTER



(*Top Right*)

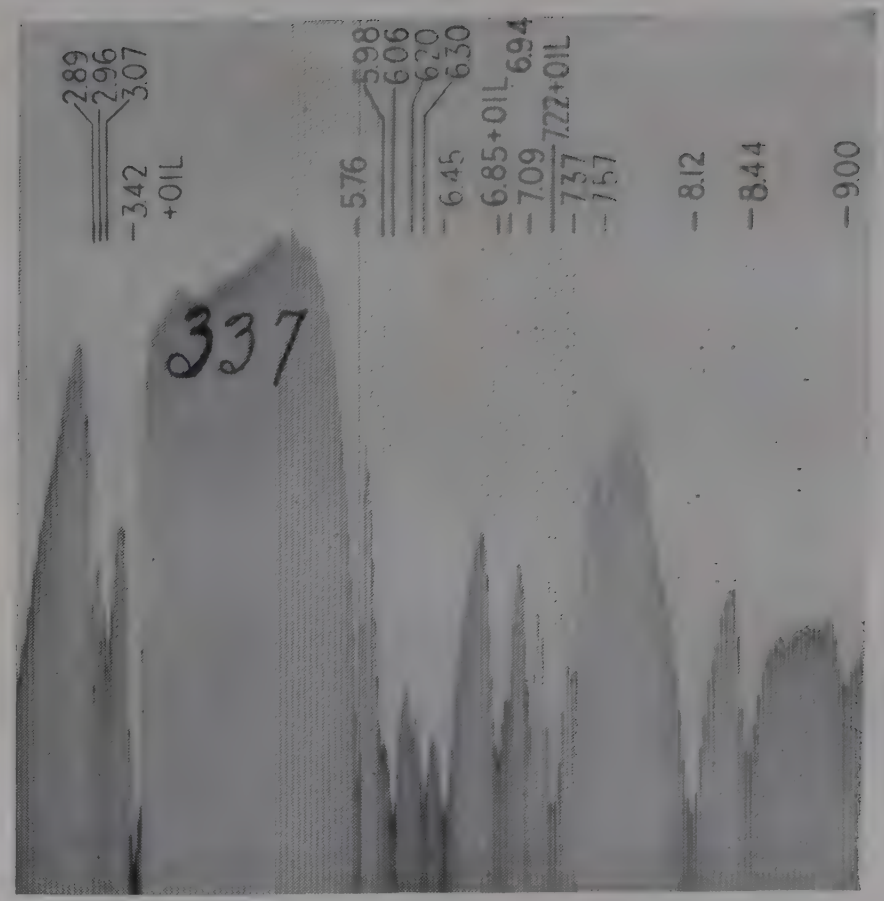


PLATE 28. 5.76 μ Ester C=O; 6.06 μ Amide I. Oil paste: 6.30 μ Unassigned (NH_2); 6.45 μ Amide II.

OXALIC ACID DIETHYL ESTER
(*Bottom*)

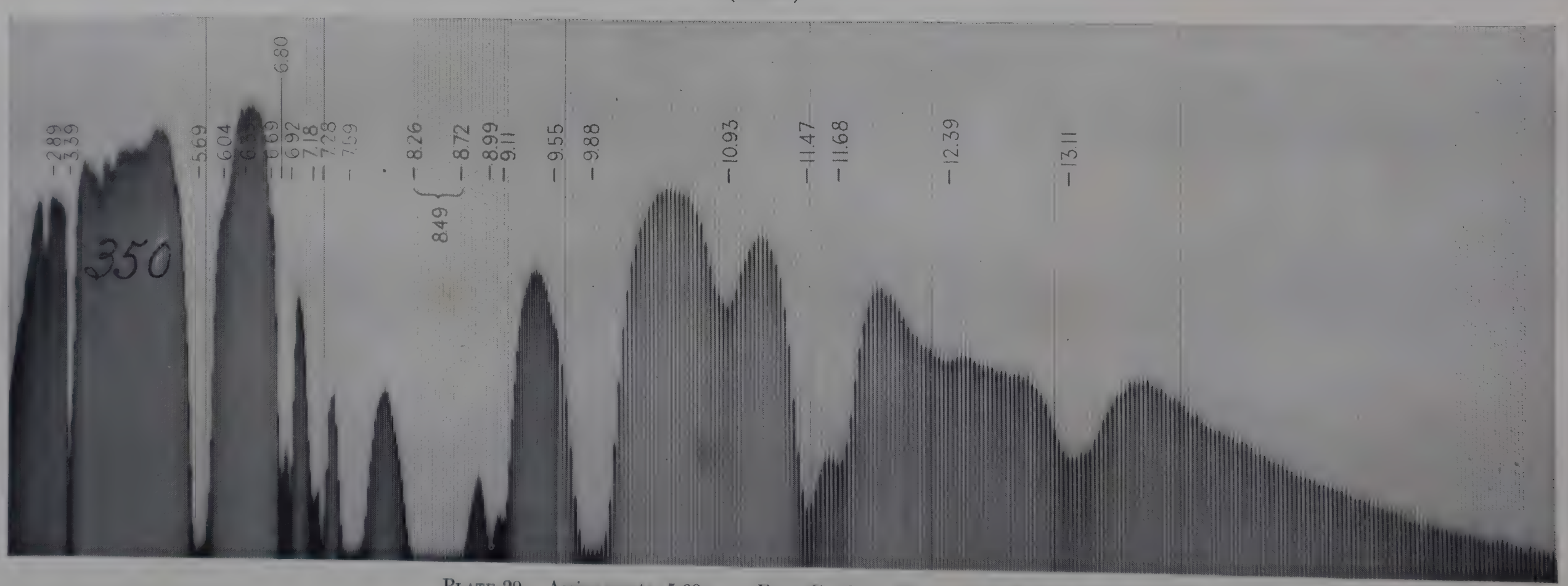


PLATE 29. Assignments: 5.69 μ Ester C=O Preparation: 0.02 mm.

SUCCINIC ACID DIETHYL ESTER

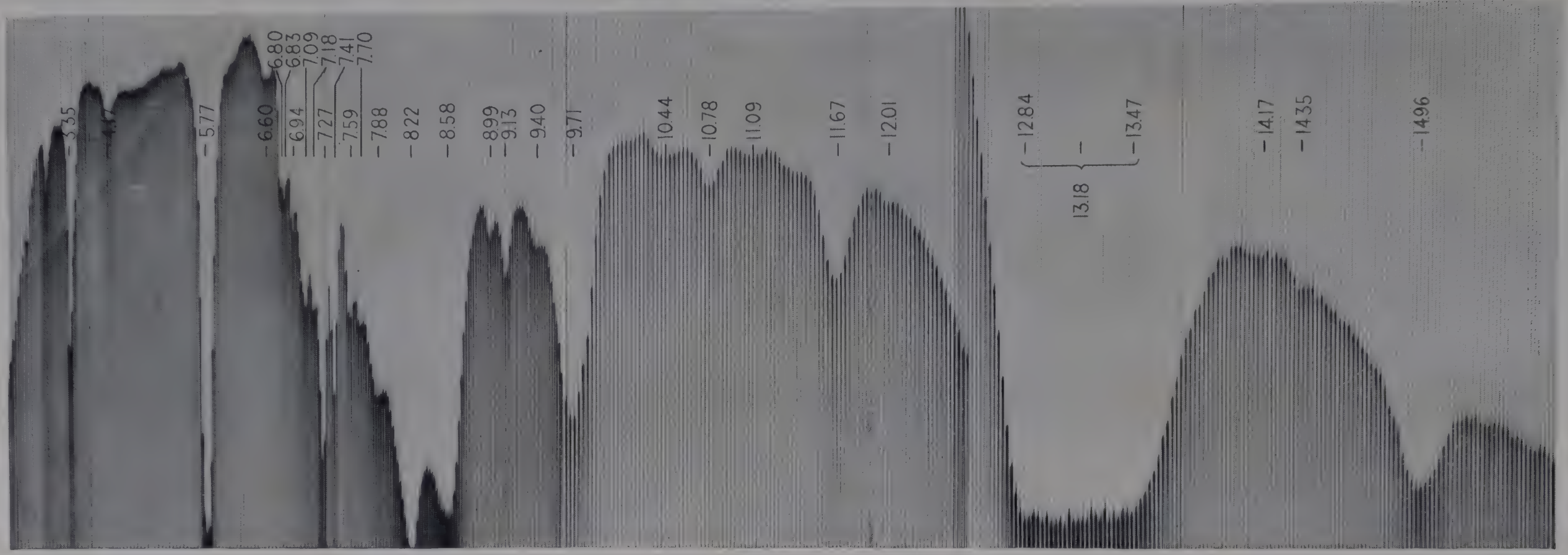
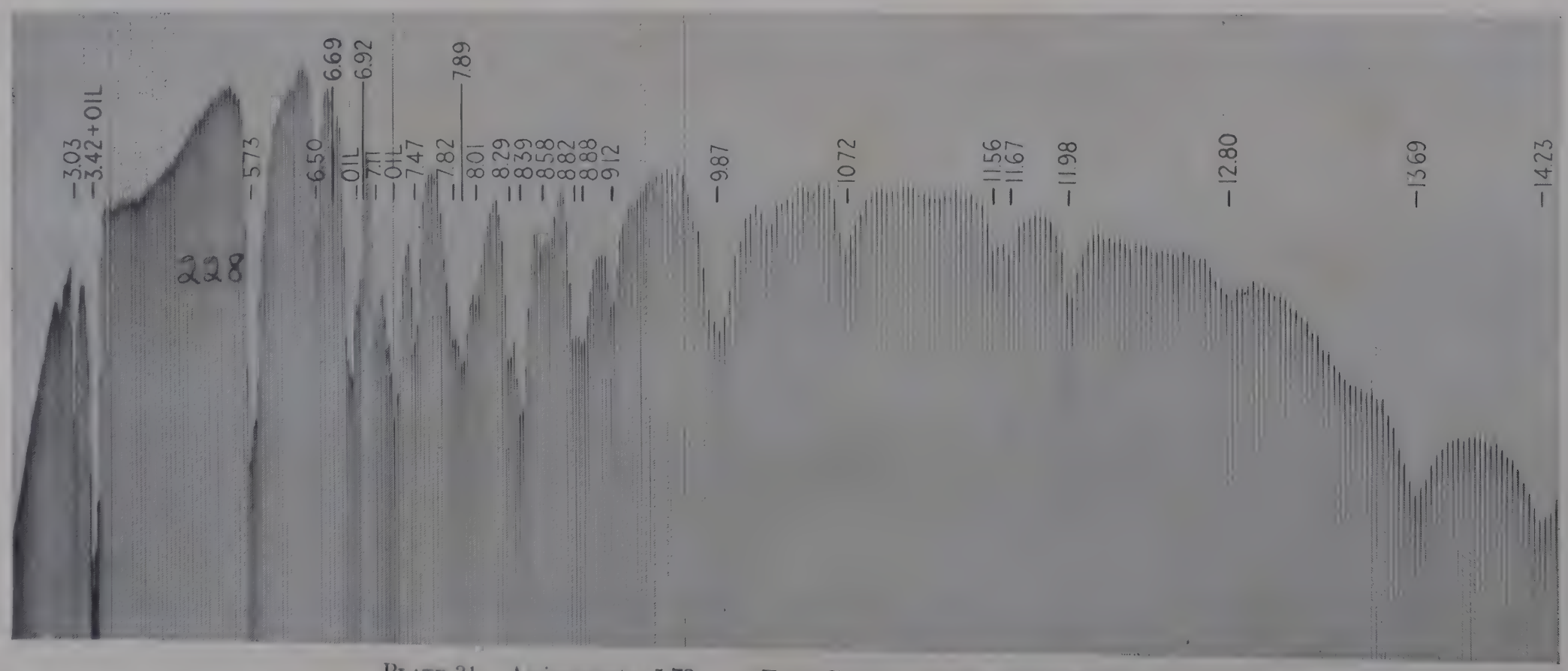


PLATE 30. Assignments: 5.77 μ Ester C=O Preparation: 0.02 mm.



THIOPHENACETAMIDOMALONIC ACID DIETHYL ESTER

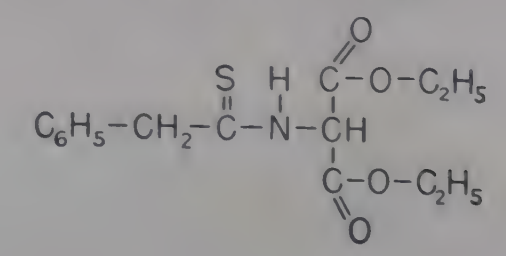


PLATE 31. Assignments: 5.73 μ Ester C=O Preparation: Oil paste

BENZOIC ACID METHYL ESTER

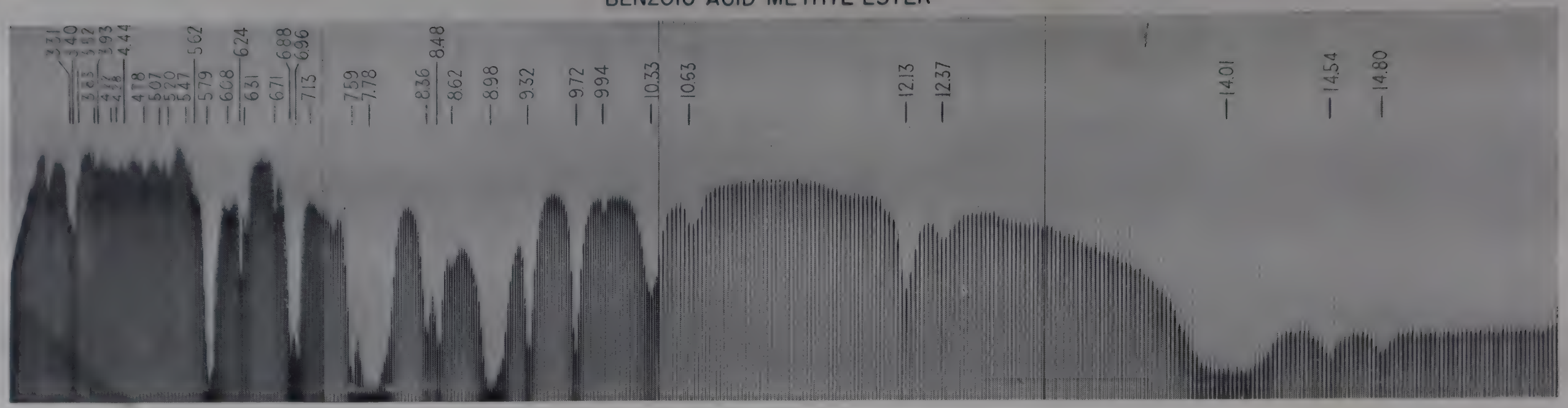


PLATE 32. Assignments: 5.79 μ Ester C=O (conjugated) Preparation: 0.15 mm.
6.24 μ, 6.31 μ, 6.71 μ Conjugated phenyl

FORMIC ACID ETHYL ESTER

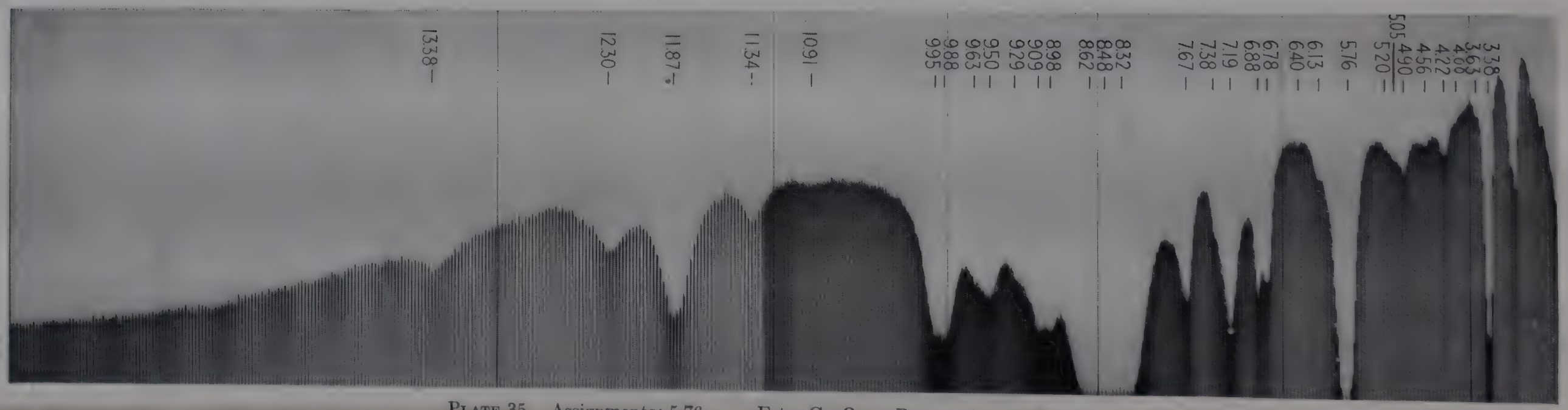


PLATE 35. Assignments: 5.76 μ Ester C=O Preparation: 0.15 mm.

ACETIC ACID ETHYL ESTER

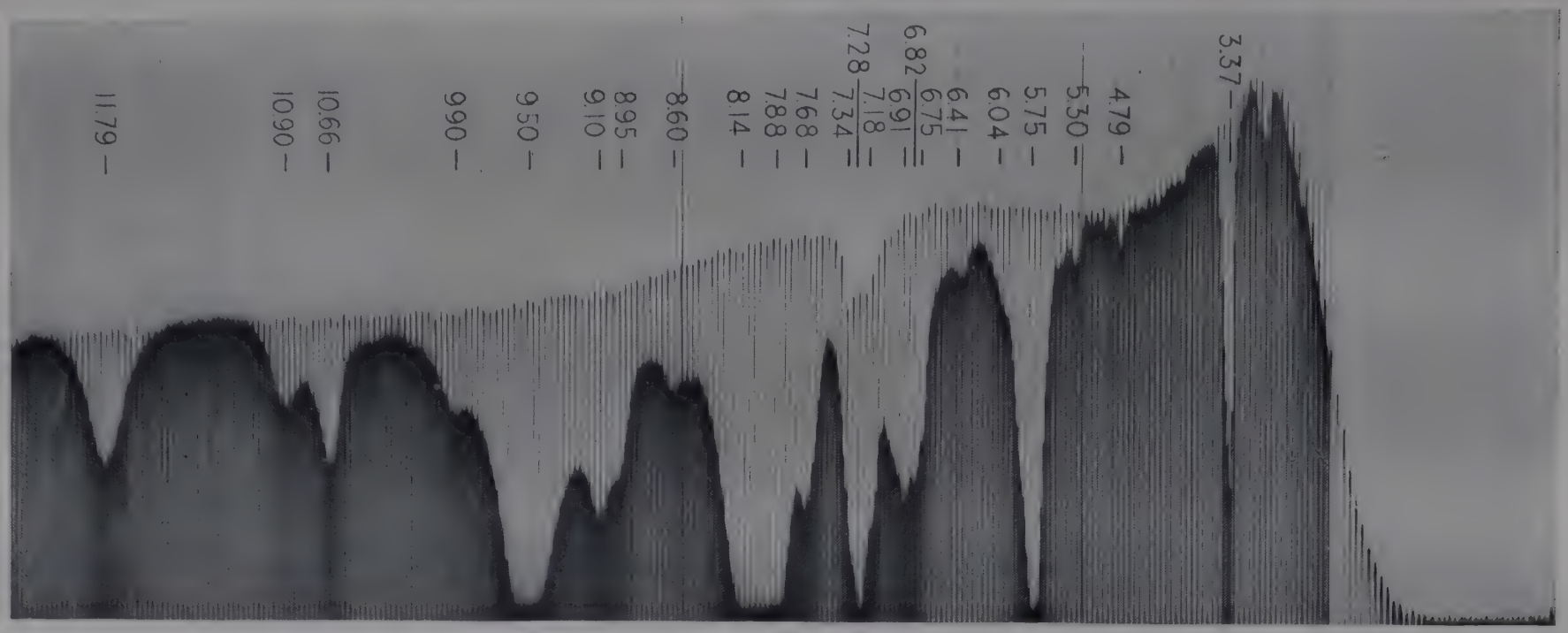


PLATE 34. Assignments: 5.75 μ Ester C=O Preparation: 0.15 mm.

ACETIC ACID BUTYL ESTER

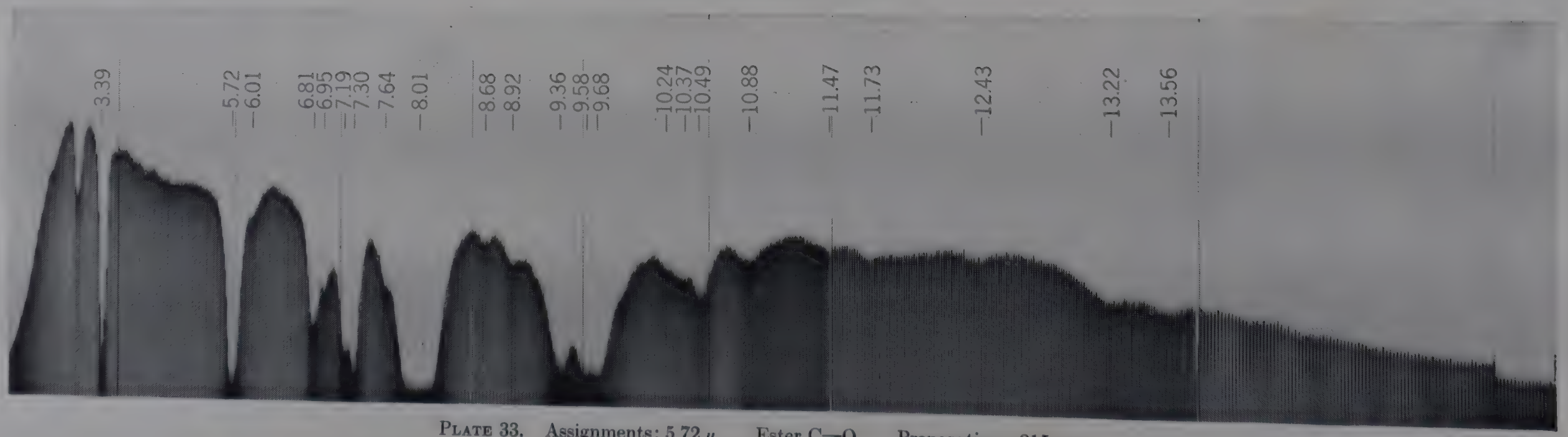


PLATE 33. Assignments: 5.72 μ Ester C=O Preparation: .015 mm.

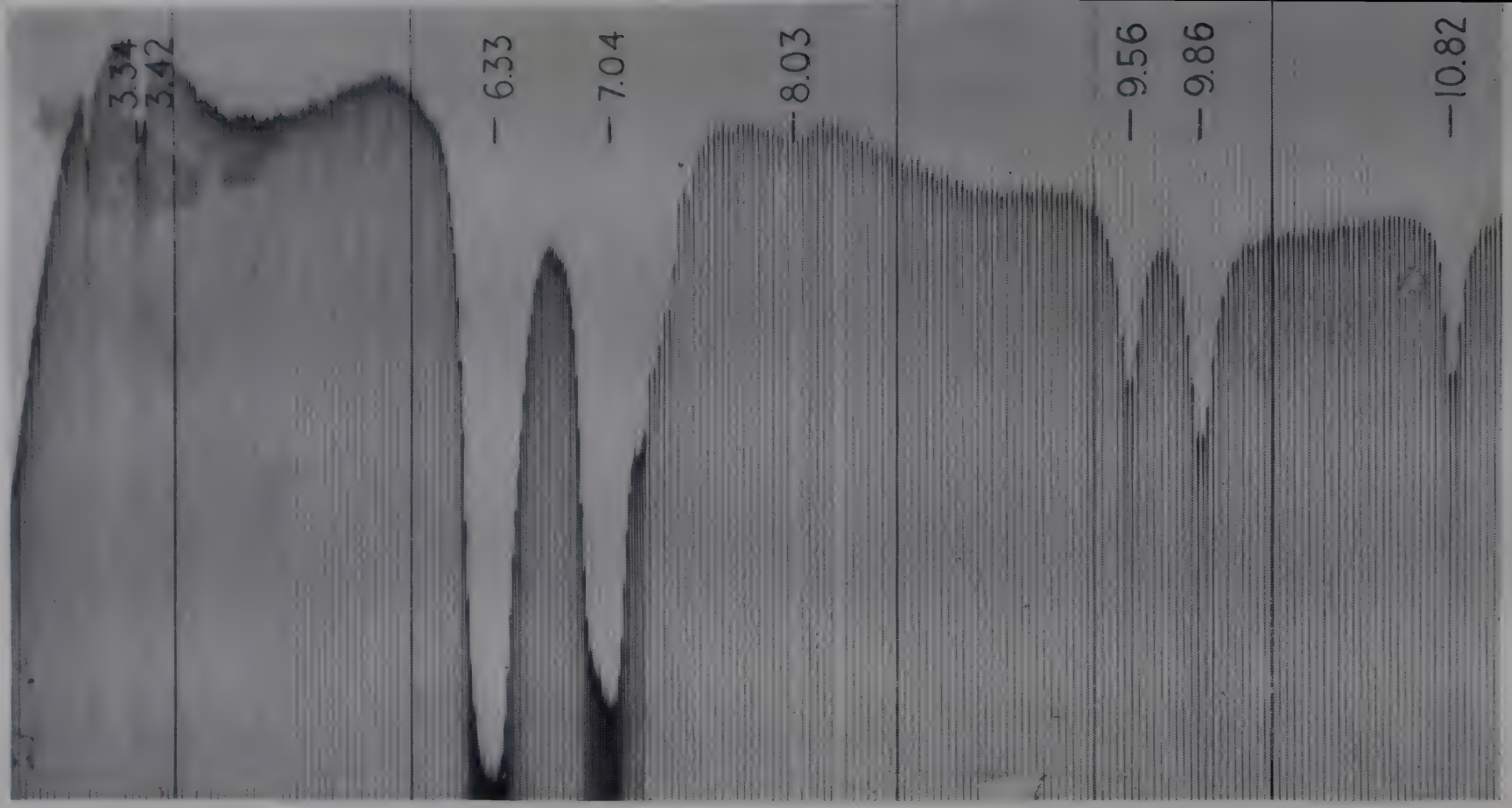


PLATE 36. Assignments: 6.33 μ Carboxylate ion Preparation: Deposited from methanol

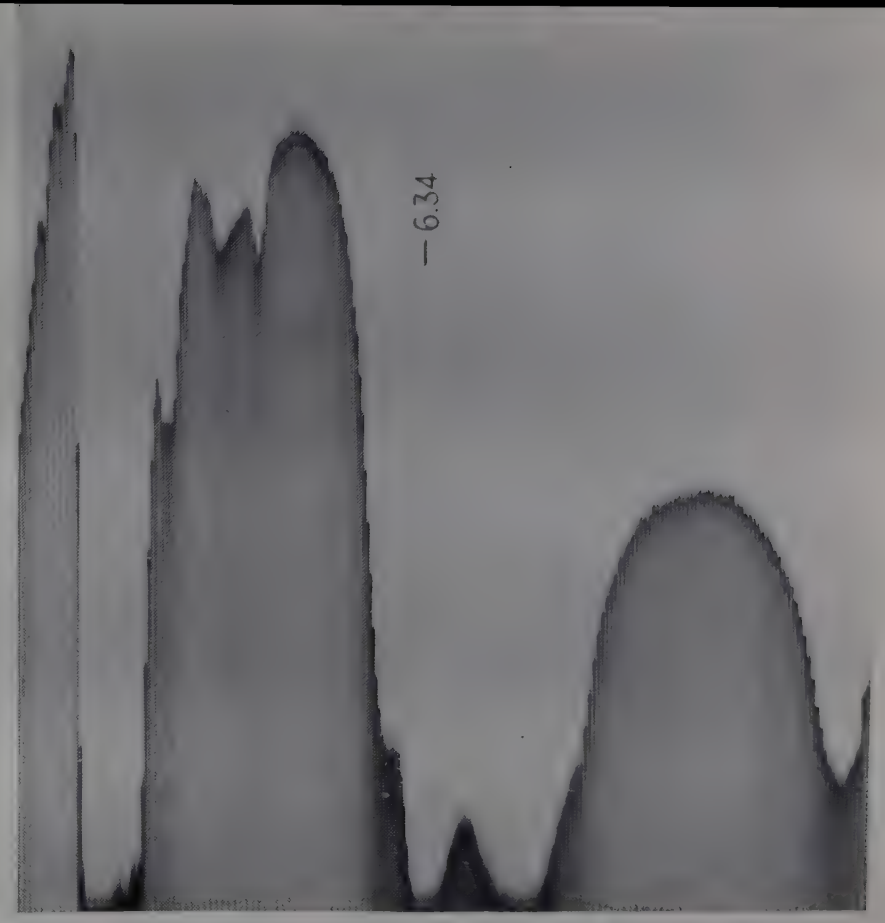


PLATE 36a. Assignments: 6.34 μ Carboxylate ion
Preparation: Methanol solution 0.02 mm.

SODIUM BICARBONATE

Na H CO_3

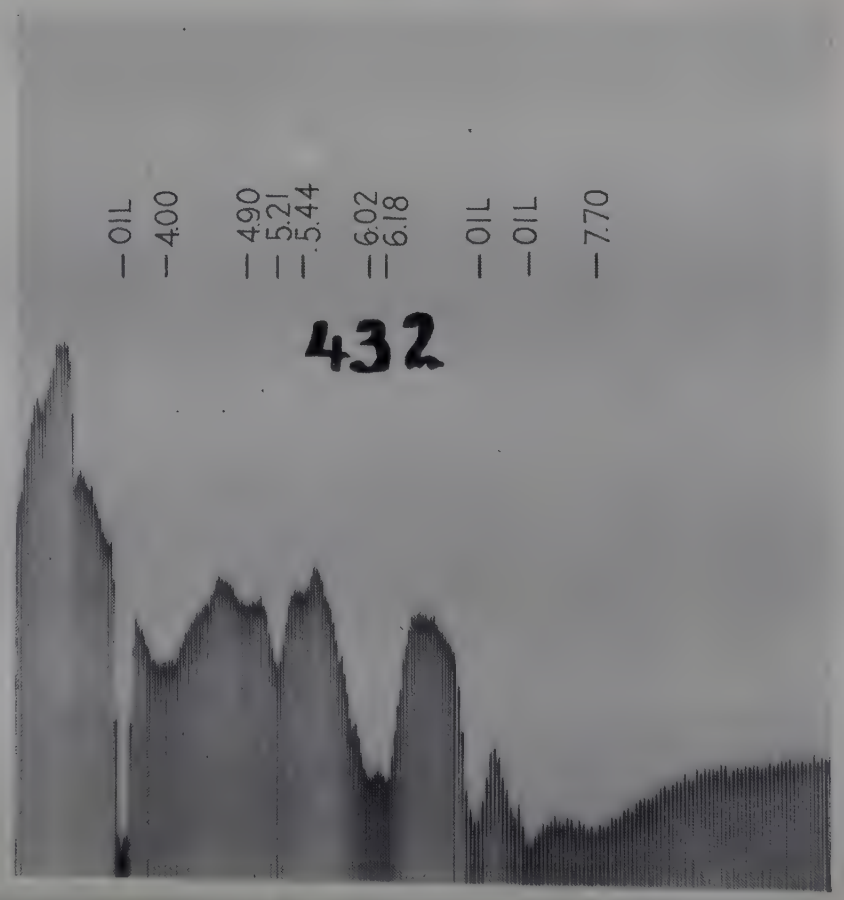


PLATE 38. Preparation: Oil paste

N-ACETYLTHIAZOLIDINE-4-CARBOXYLIC ACID SODIUM SALT (HYDRATE)

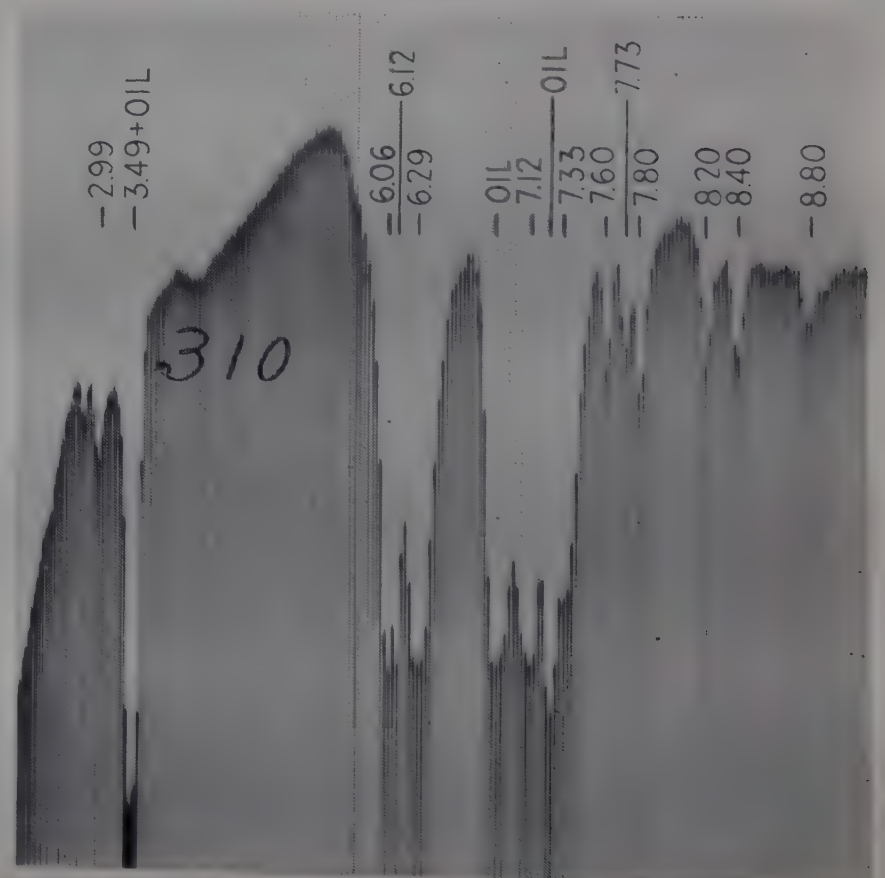


PLATE 39. 6.06 μ N-acyl C=O; 6.12 μ H$_2$O

N-PHENYLGLYCINE POTASSIUM SALT

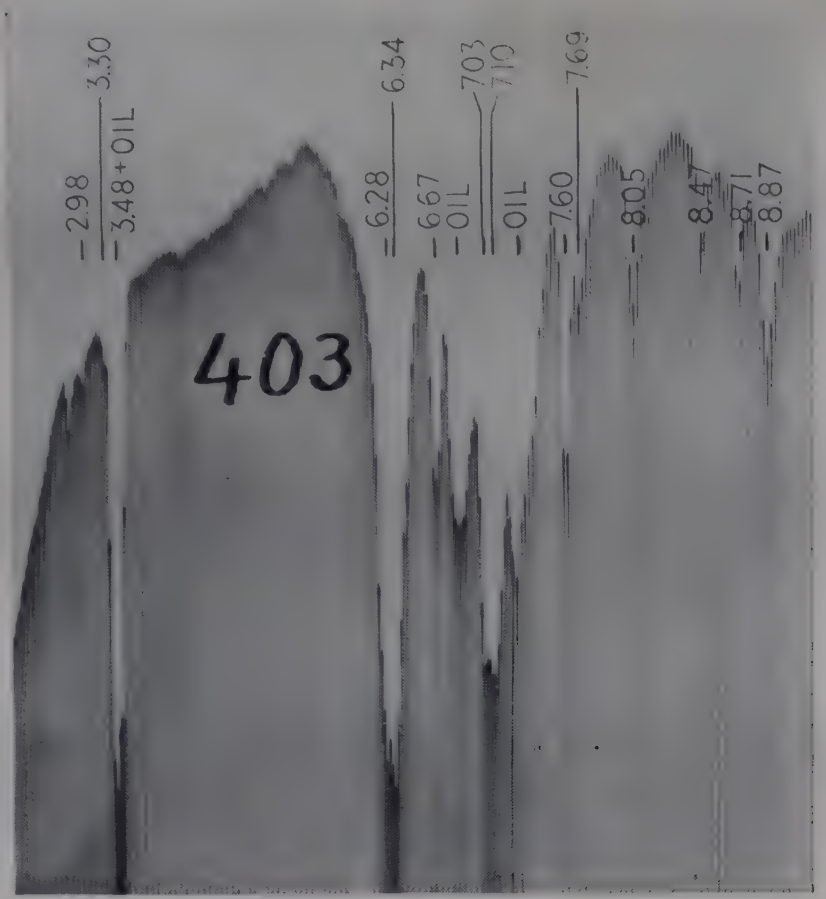


PLATE 40. Assignments: 6.28 μ Phenyl
6.34 μ Carboxylate ion plus anilino
6.67 μ Anilino
Preparation: Oil paste

ϵ-BENZAMIDOCAPROIC ACID SODIUM SALT

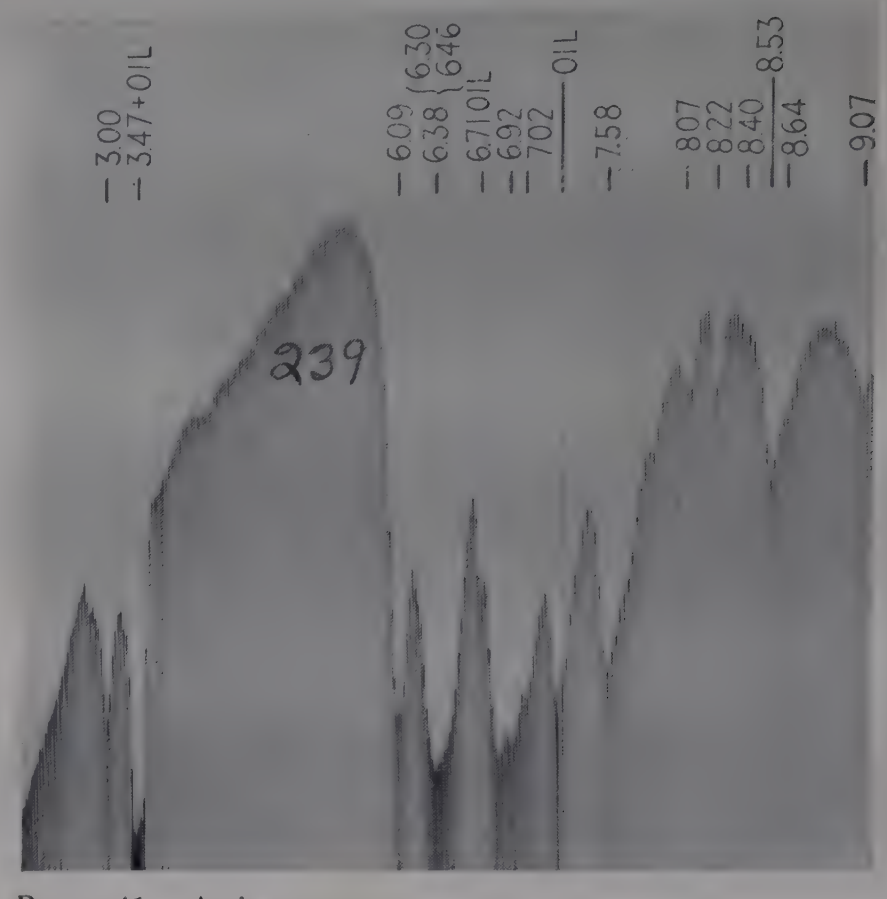


PLATE 41. Assignments:
6.09 μ Amide I
6.38 μ (Double) amide II plus carboxylate ion
6.71 μ Phenyl
Preparation: Oil paste

PHENACETAMIDOMALONIC ACID
MONO-ETHYL ESTER SODIUM SALT

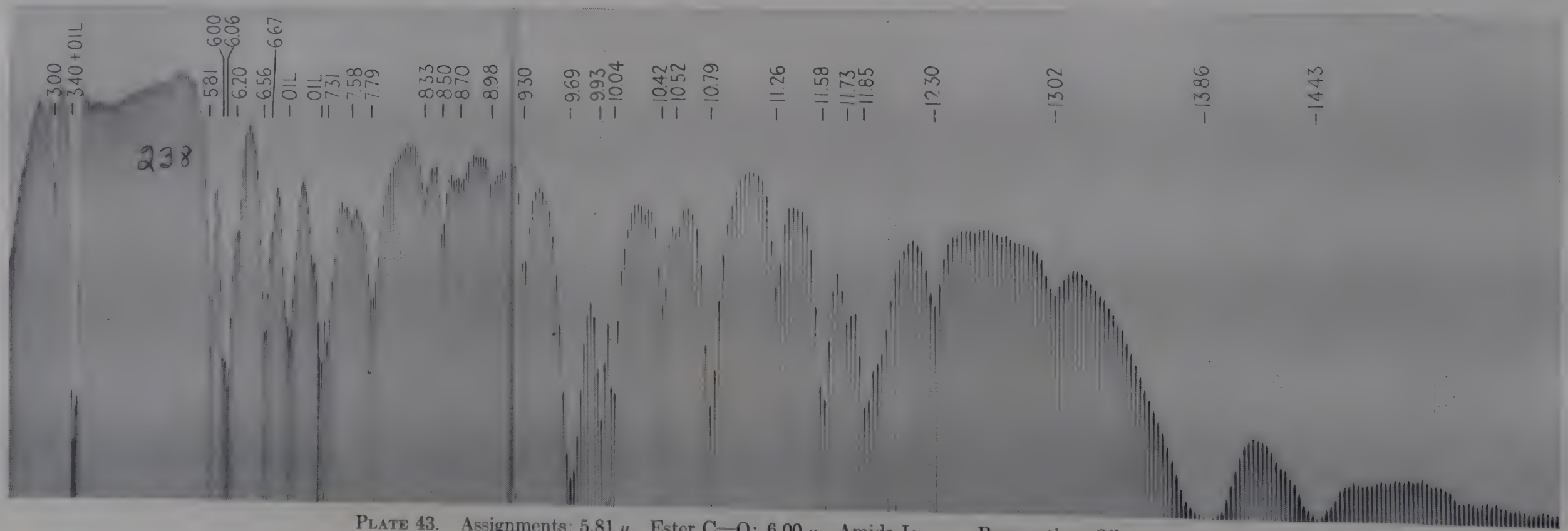


PLATE 43. Assignments: 5.81 μ Ester C=O; 6.00 μ Amide I;
6.06 μ Carboxylate ion; 6.20 μ Phenyl
Preparation: Oil paste

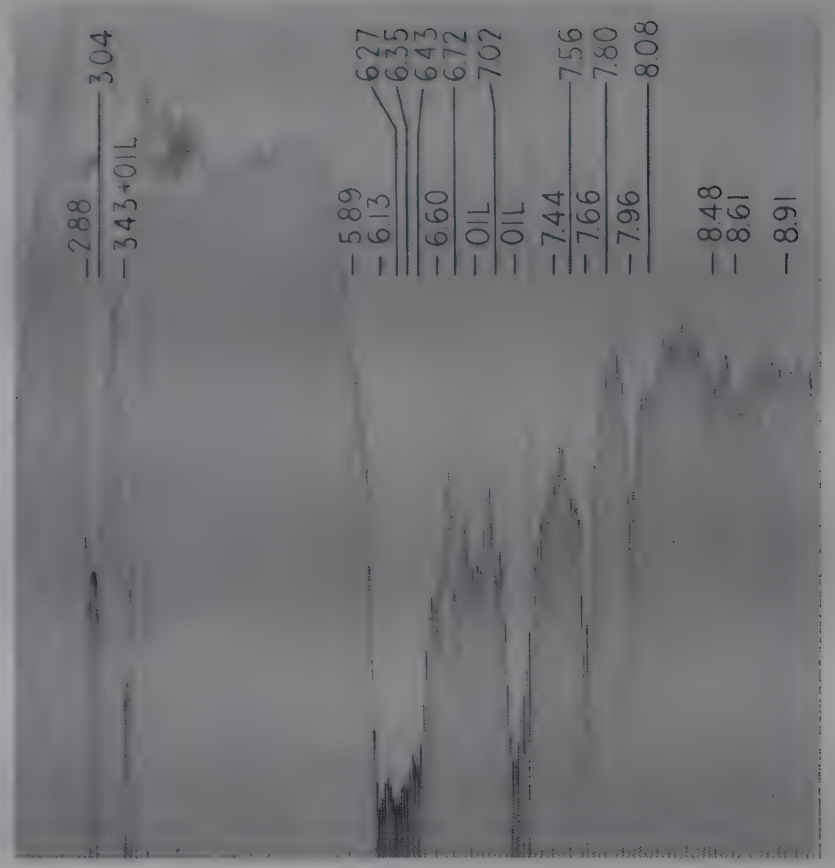


PLATE 42. Assignments: 6.13 μ Amide I plus H_2O
6.27 μ Carboxylate ion
6.27 μ, 6.35 μ, 6.72 μ Conjugated phenyl
6.43 μ Amide II
Preparation: Oil paste

PLATE 48. Assignments:
6.04 μ Amide I
6.19 μ H_2O
6.30 μ Carboxylate ion
6.60 μ Amide II
Preparation: Oil paste

dl-N-PHENACETYLALANINE SODIUM SALT

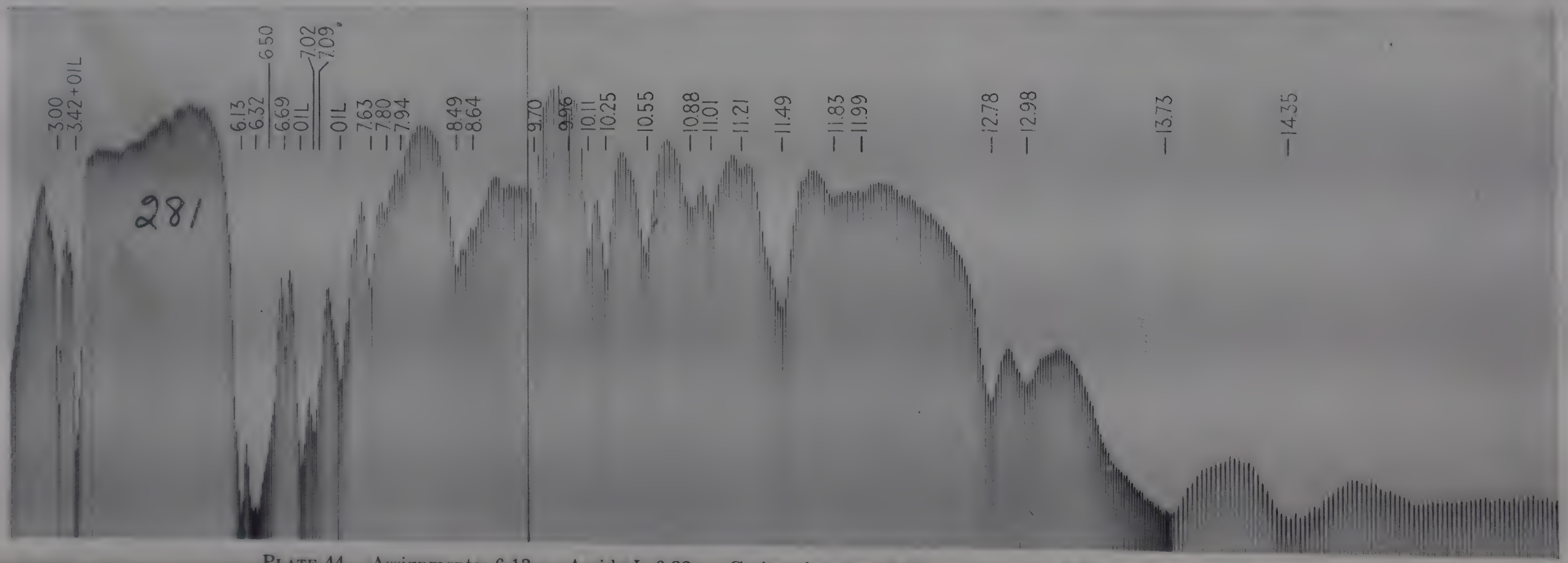


PLATE 44. Assignments: 6.13 μ Amide I; 6.32 μ Carboxylate ion; 6.50 μ Amide II; 6.69 μ Phenyl. Oil paste

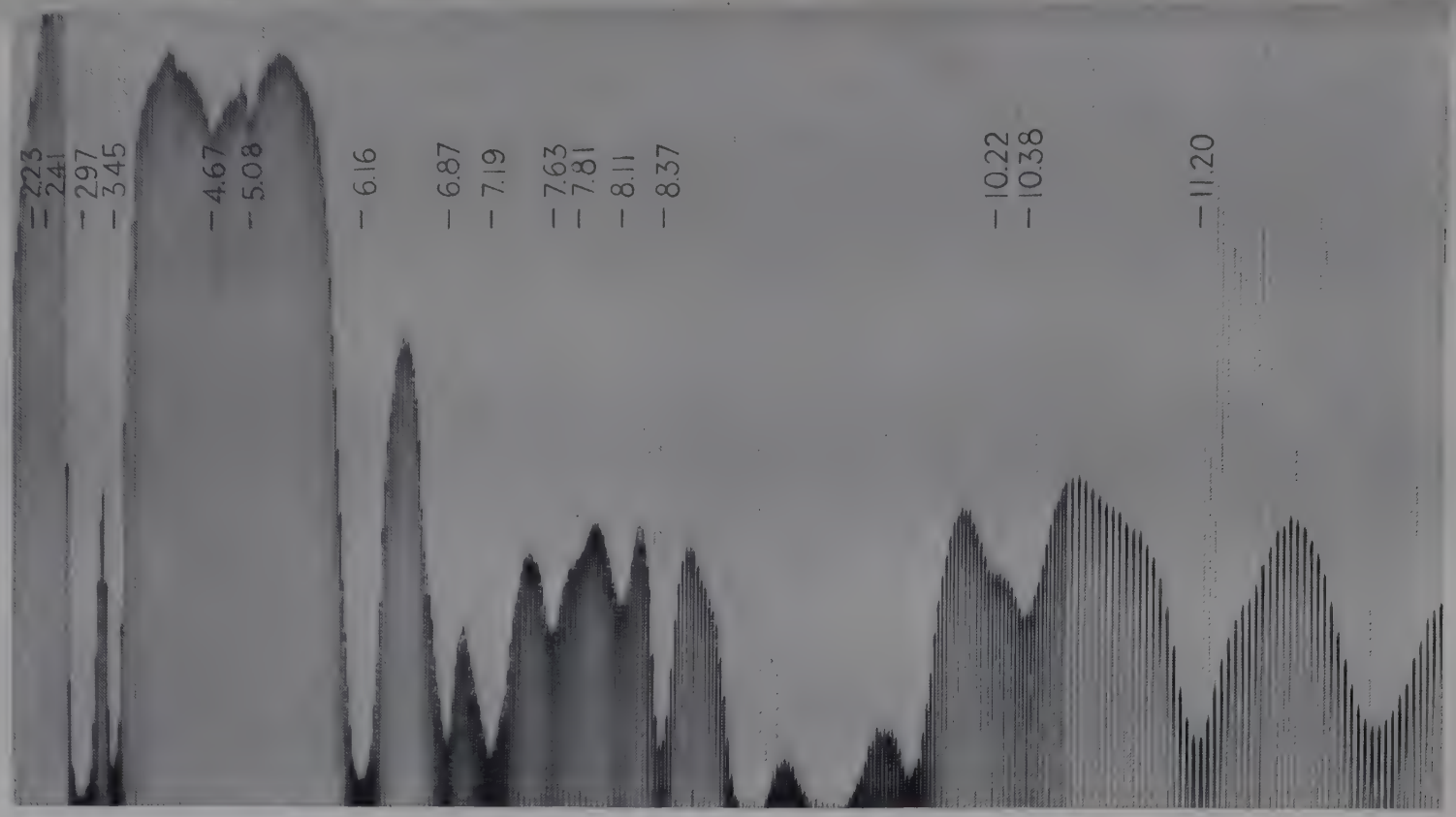


PLATE 45a. Assignments: 6.16 μ { Amide I / Carboxylate ion
Bands not measured—methanol

Preparation: Methanol solution, 0.02 mm.

N-PHENACETYLSARCOSINE SODIUM SALT
(*Bottom and Left*)

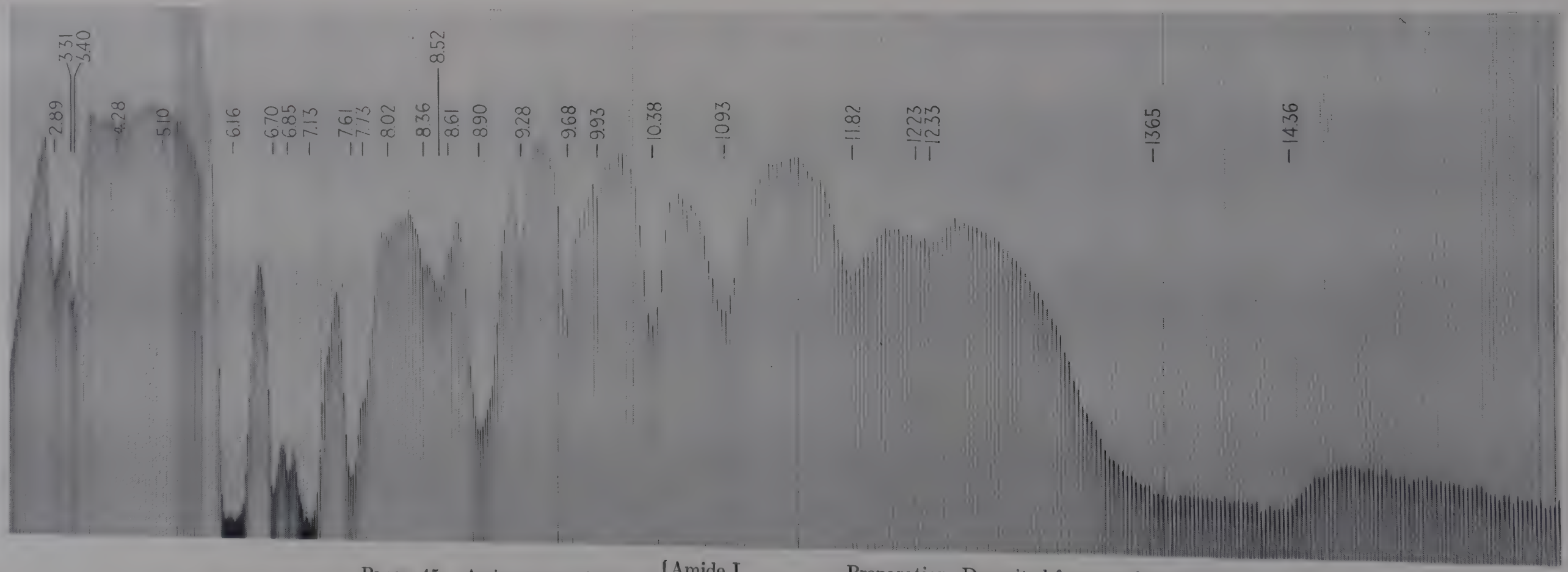


PLATE 45. Assignments: 6.16 μ { Amide I / Carboxylate ion
6.70 μ Phenyl

Preparation: Deposited from methanol

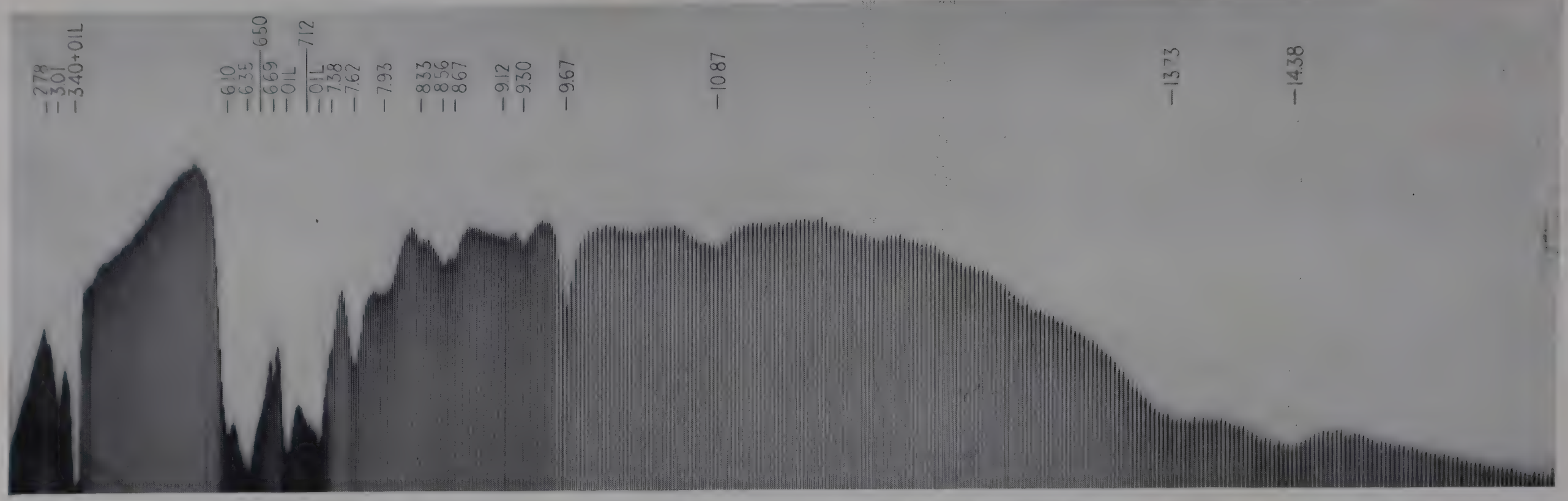


PLATE 46. Assignments: 6.10 μ Amide I; 6.35 μ Carboxylate ion; 6.50 μ Amide II. Preparation: Oil paste

PHENACETURIC ACID BARIUM SALT (HEXAHYDRATE)

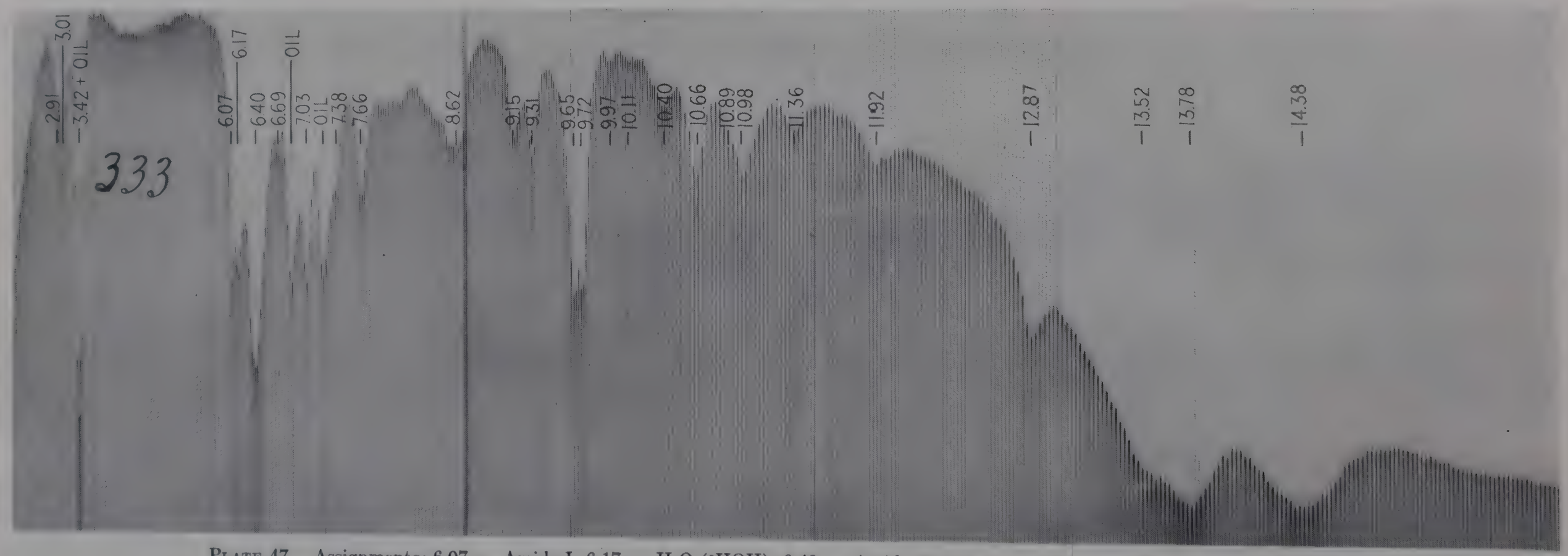


PLATE 47. Assignments: 6.07 μ Amide I; 6.17 μ H_2O (δHOH); 6.40 μ Amide II plus carboxylate ion. Preparation: Oil paste

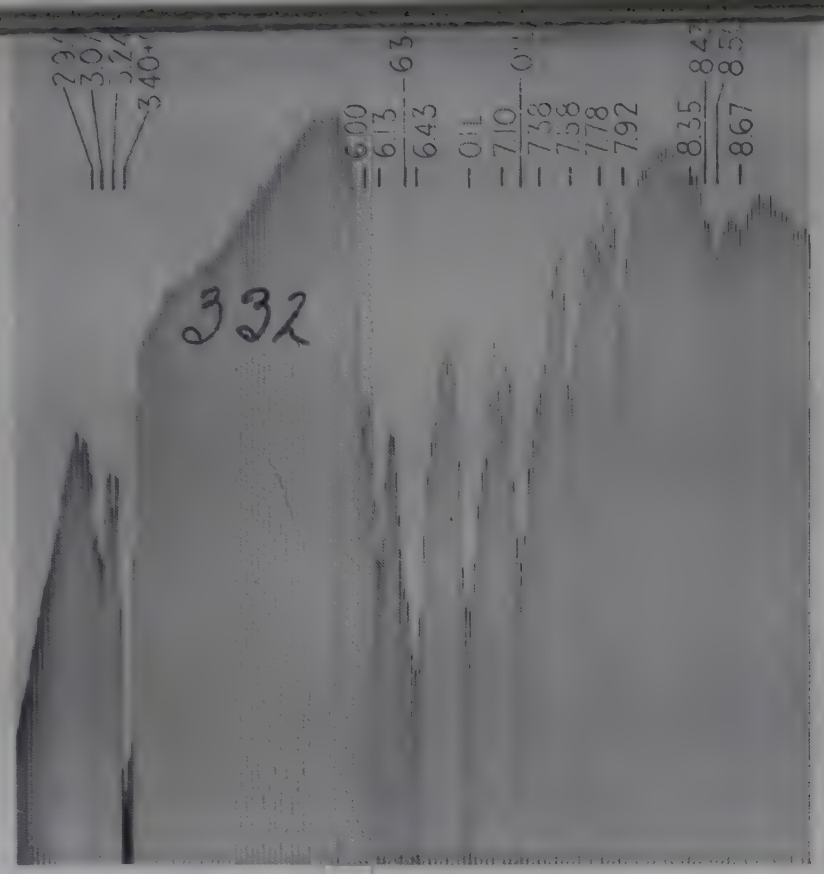
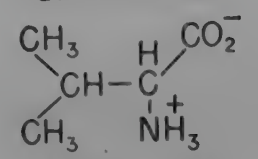


PLATE 49. Assignments: 6.00 μ Amide I
6.13 μ H_2O (δHOH)
6.34 μ Carboxylate ion
6.43 μ Amide II
Preparation: Oil paste

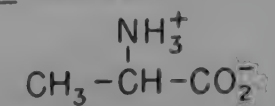
(*Top Left*)

dl–VALINE



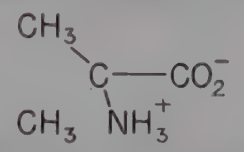
(*Bottom Left*)

dl–ALANINE



(*Top Right*)

α–AMINOISOBUTYRIC ACID



(*Bottom Center and Right*)

PLATE 50. Assignments: 6.17 μ Amino acid I (δNH_3^+)
6.29 μ Carboxylate ion
6.57 μ Amino acid II
Preparation: Oil paste

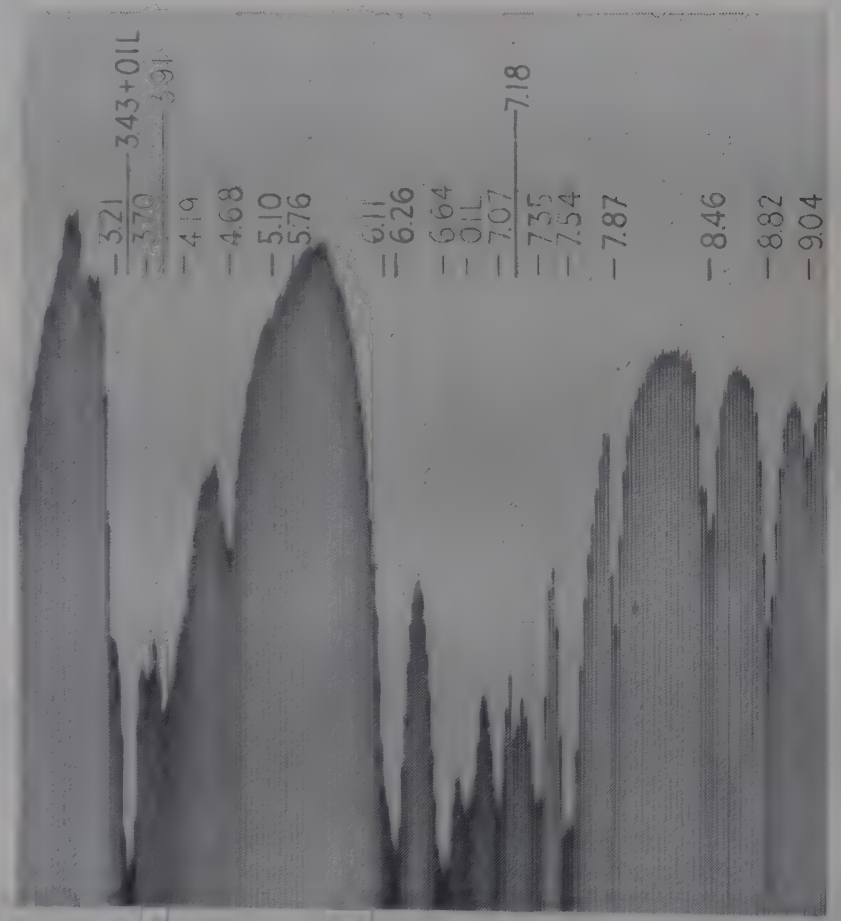


PLATE 51. Assignments: 6.11 μ Amino acid I (δNH_3^+)
6.26 μ Carboxylate ion
6.64 μ Amino acid II

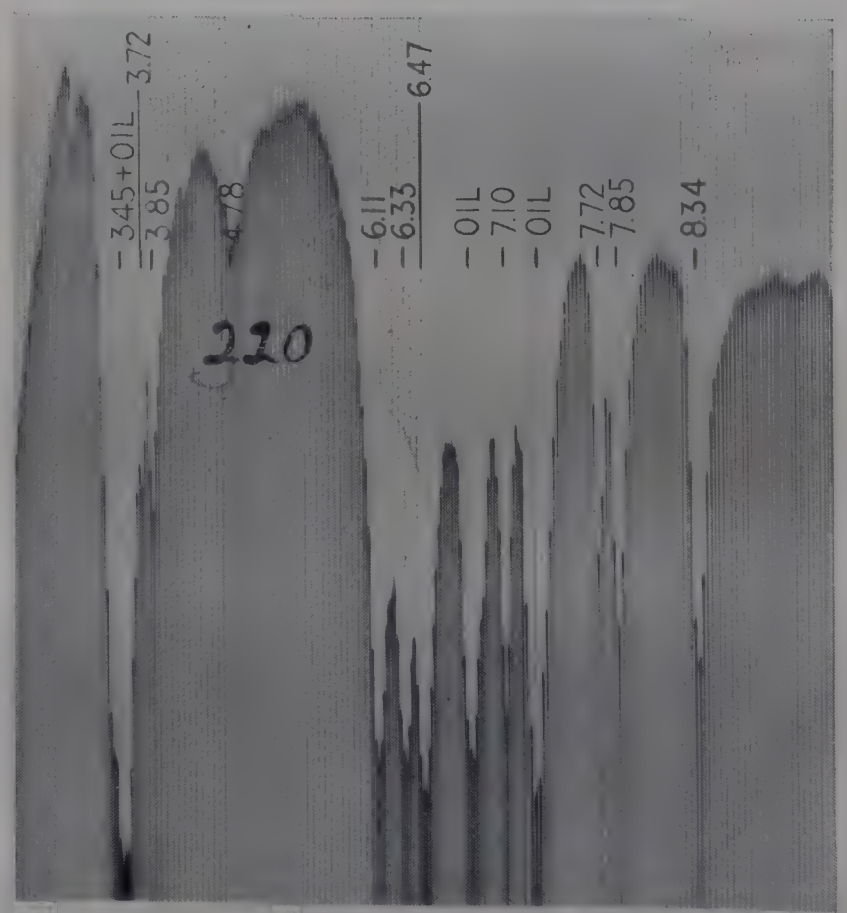


PLATE 52. Assignments: 6.11 μ Amino acid I (δNH_3^+)
6.33 μ Carboxylate ion

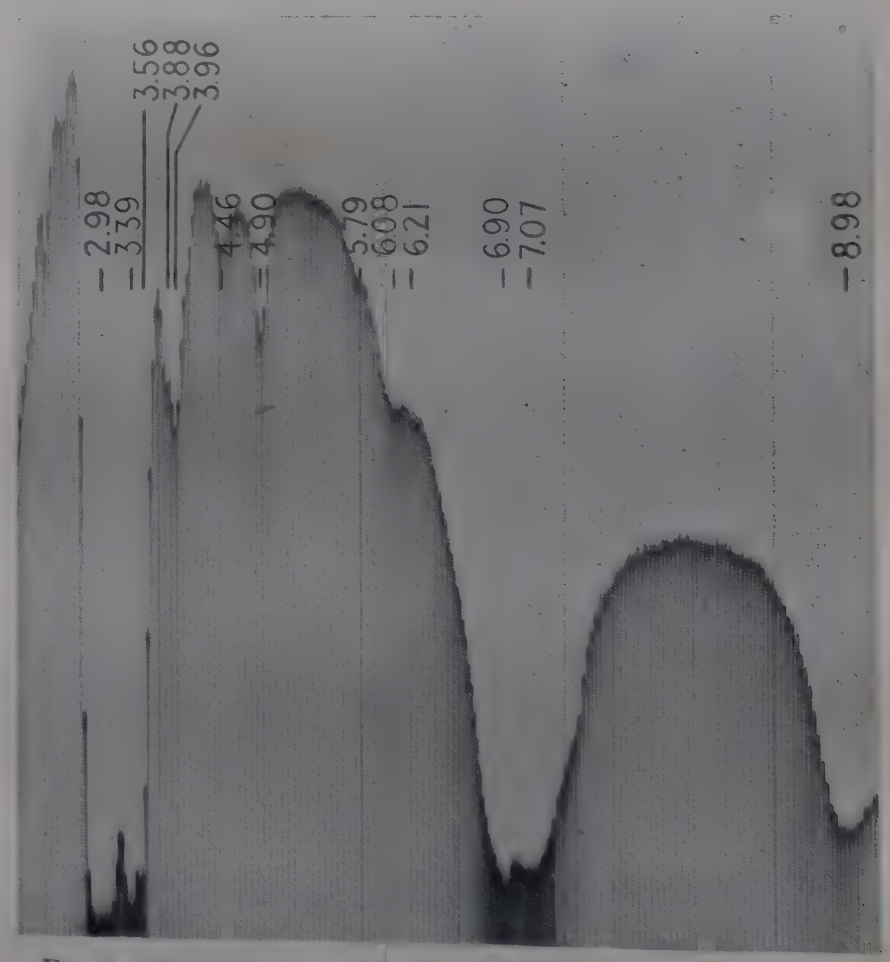


PLATE 52a. Preparation: Methanol solution, 0.02 mm.

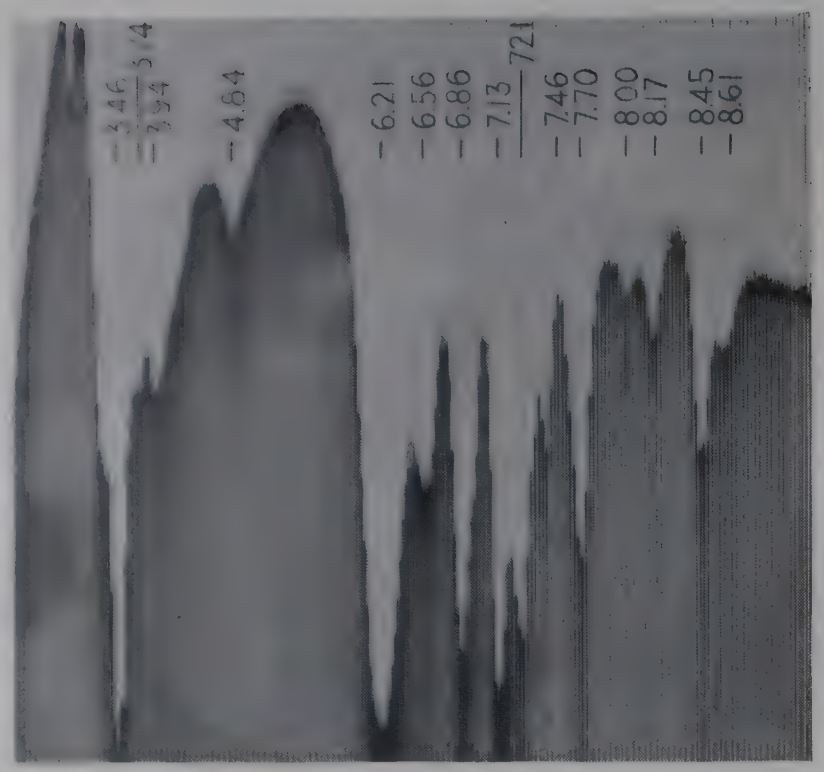


PLATE 53. Assignments: 6.21 μ (δNH_3^+), carboxylate ion
6.56 μ Amino acid II
Preparation: Oil paste

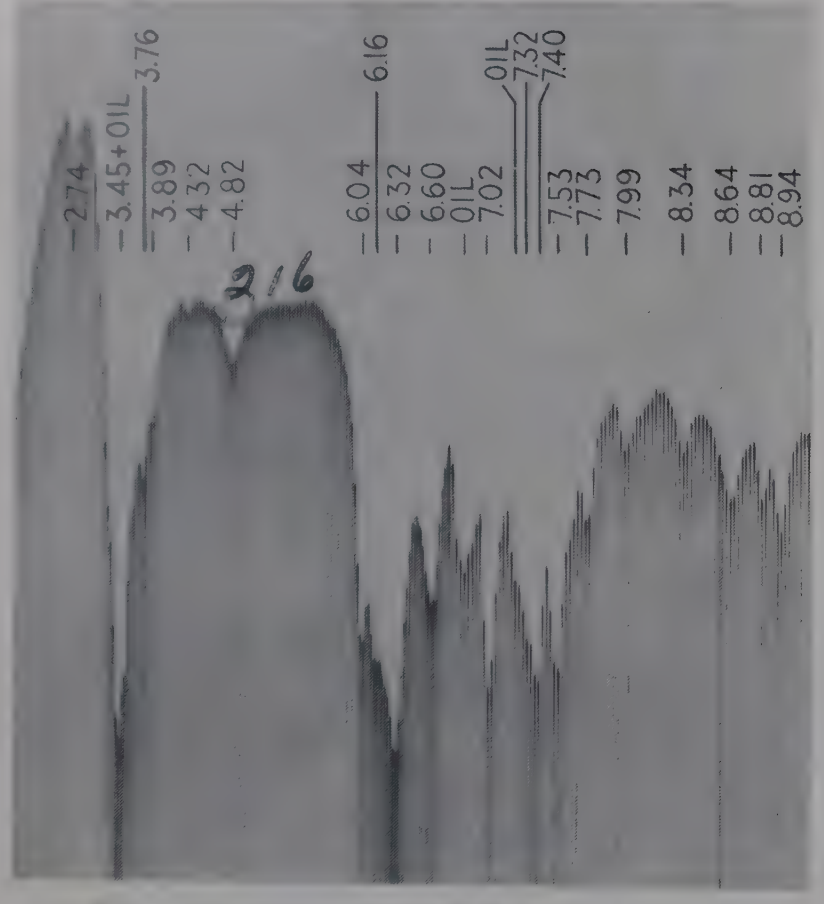


PLATE 54. Assignments: 6.04 μ Unassigned;
6.16 μ Amino acid I (δNH_3^+); 6.32 μ Carboxylate ion;
6.60 μ Amino acid II. Oil paste

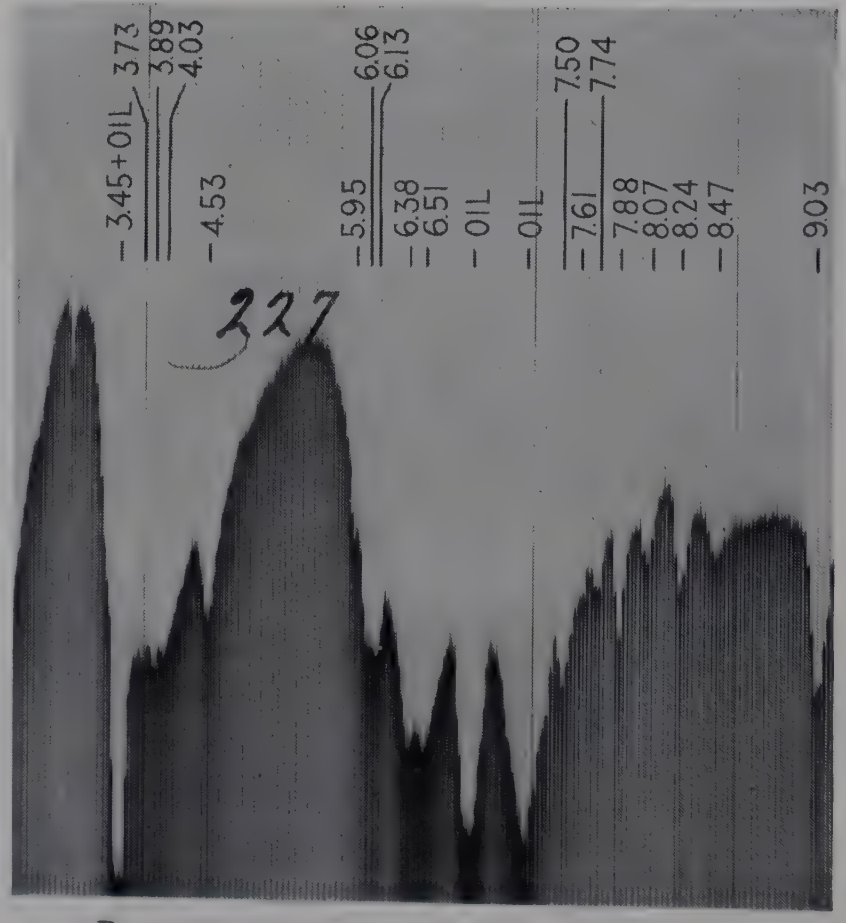


PLATE 55. Assignments: 5.95 μ Unassigned;
6.13 μ Amino acid I (δNH_3^+); 6.38 μ Carboxylate ion;
6.51 μ Amino acid II. Oil paste

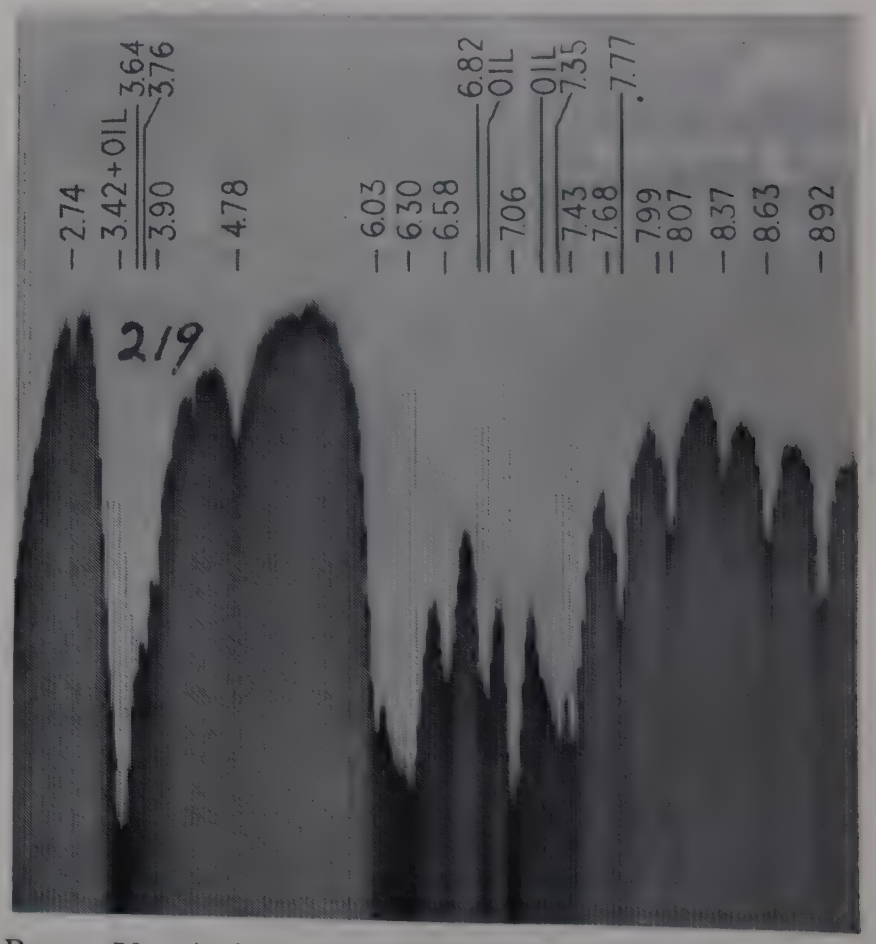


PLATE 56. Assignments: 6.03 μ Amino acid I (δNH_3^+);
6.30 μ Carboxylate ion; 6.58 μ Amino acid II. Oil paste

CH_3
$CH_3-CH_2-C-CO_2^-$
NH_3^+
(Top Left and Right)

dl-α-AMINO-n-VALERIC ACID
$C_2H_5-CH_2-CH-CO_2^-$
(NH_3^+)
(Bottom Left)

ϵ-AMINO-n-CAPROIC ACID
$H_3^+N-(CH_2)_5-CO_2^-$
(Bottom Center)

dl-α-AMINO-n-CAPROIC ACID
$CH_3-(CH_2)_3-CH$ (CO_2^-, NH_3^+)
(Bottom Right)

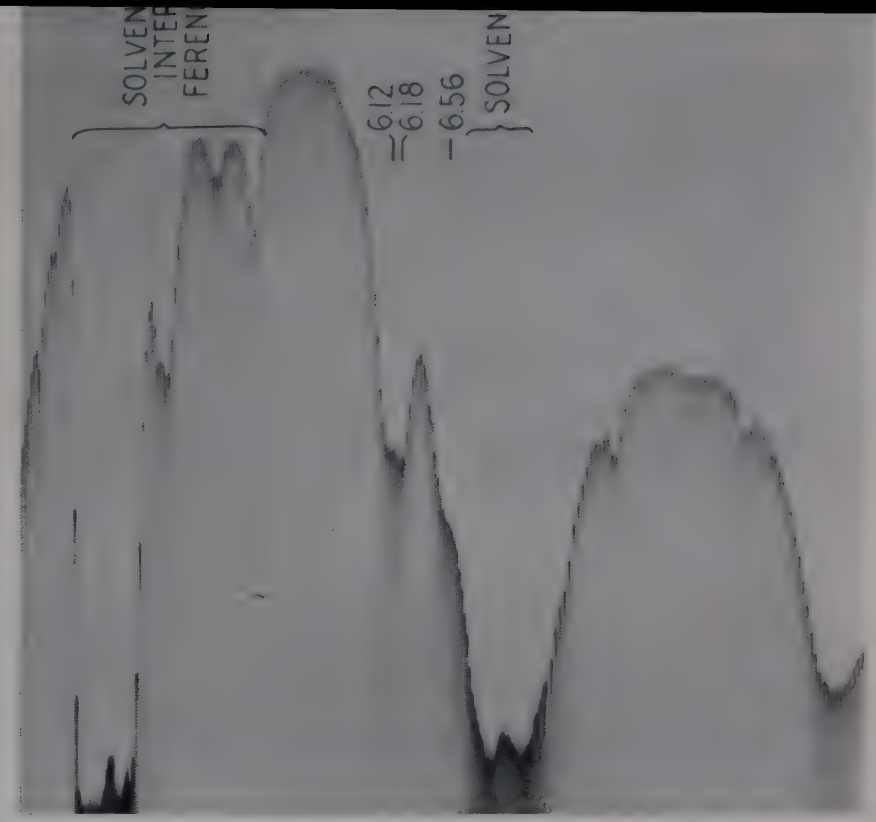


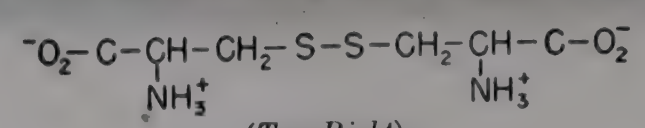
PLATE 53a. Assignments:
6.12 μ Carboxylate ion
6.18 μ Amino acid I (δNH_3^+)
6.56 μ Amino acid II
Preparation: Methanol solution, 0.02 mm.

PLATE 57. Assignments:

5.92 μ	Acid C=O
6.18 μ	(δNH_3^+), carboxylate ion
6.67 μ	Amino acid II

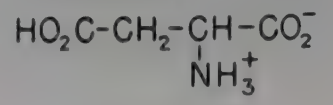
Preparation: Oil paste

CYSTINE



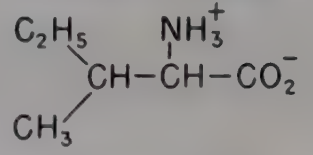
(*Top Right*)

dl-ASPARTIC ACID



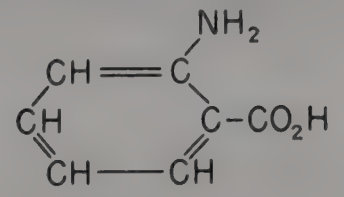
(*Top Left*)

d-ISOLEUCINE



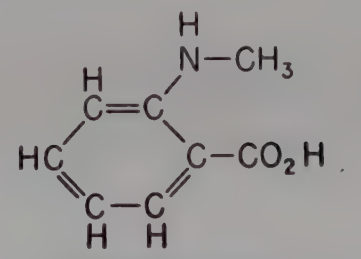
(*Bottom Left*)

ANTHRANILIC ACID



(*Bottom Center*)

N-METHYL ANTHRANILIC ACID



(*Bottom Right*)

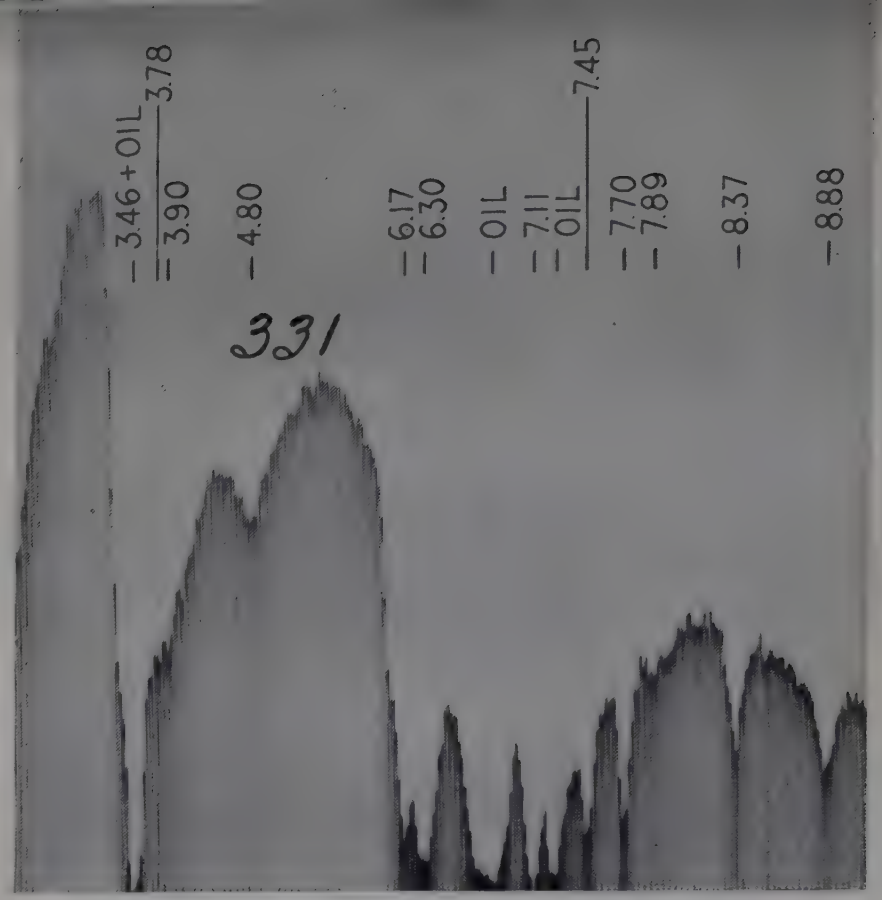


PLATE 58. Assignments: 6.17 μ δNH_3^+
6.30 μ Carboxylate ion
Preparation: Oil paste

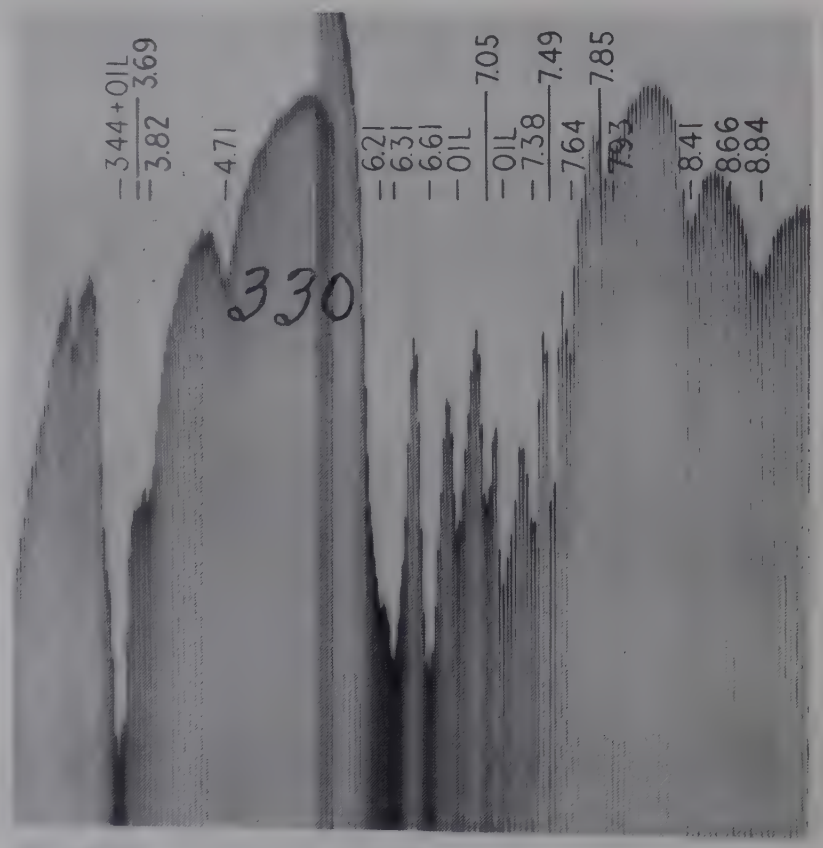


PLATE 59. Assignments: 6.21 μ Amino acid I (δNH_3^+)
6.31 μ Carboxylate ion
6.61 μ Amino acid II
Preparation: Oil paste

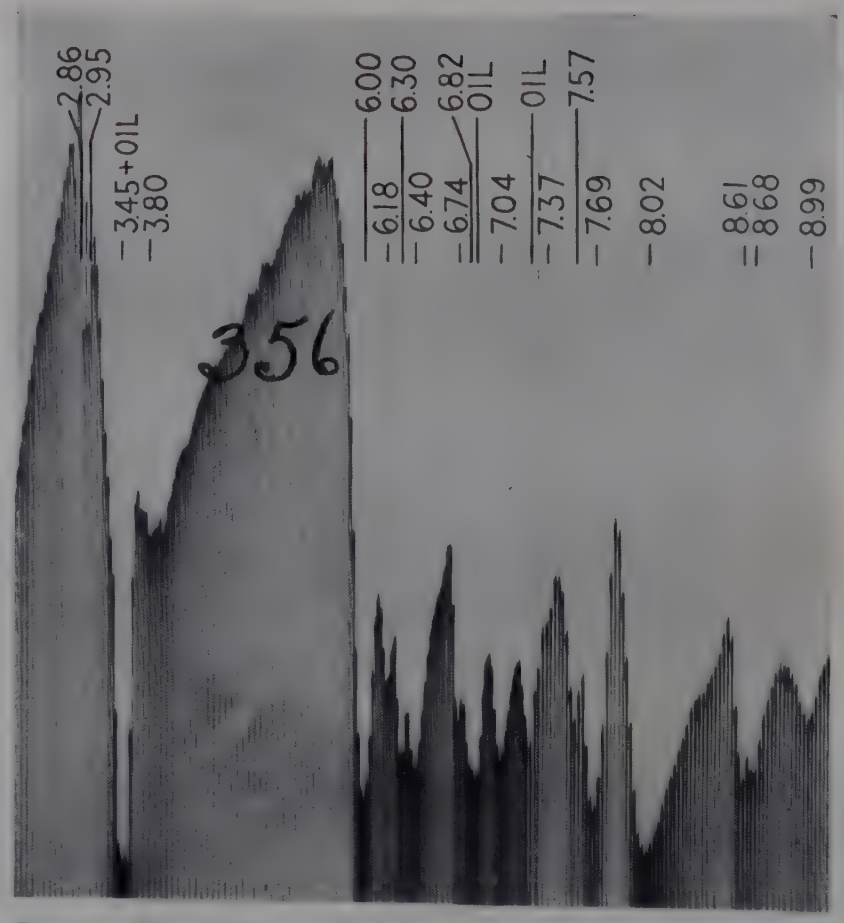


PLATE 60. 6.00 μ Conj. acid C=O; 6.18 μ δNH_2; 6.30 μ, 6.74 μ Phenyl; 6.40 μ Anilino. Oil paste.

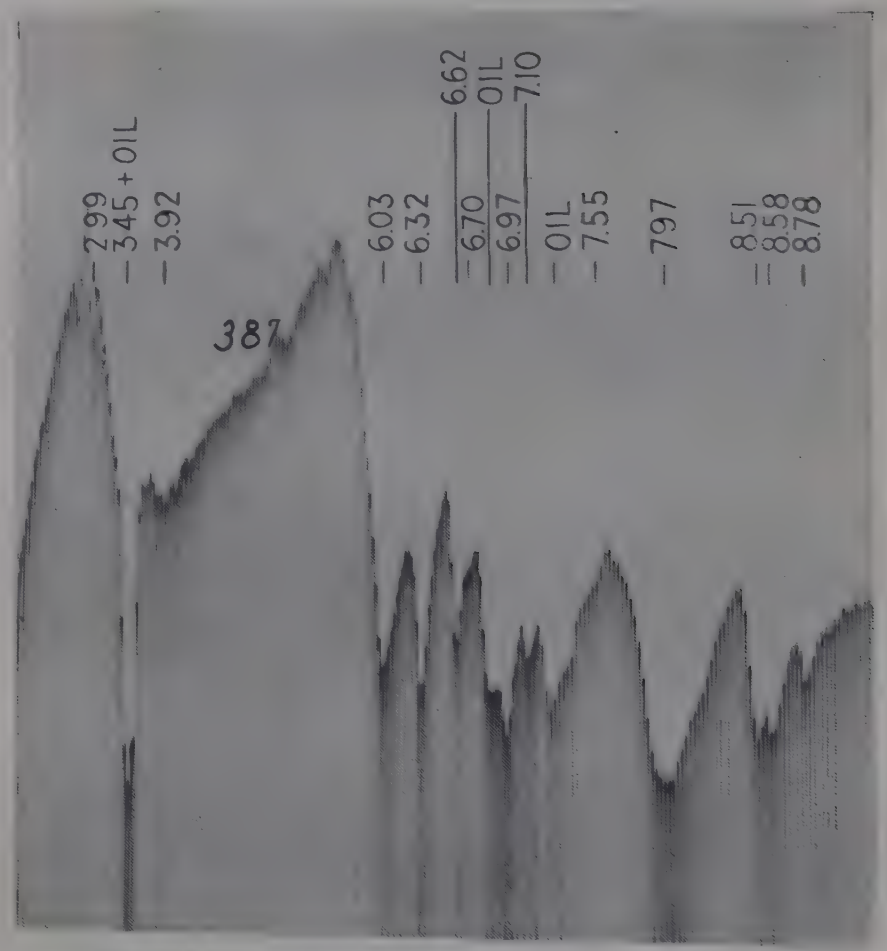


PLATE 61. Assignments:

6.03 μ	Acid C=O (conjugated)
6.32 μ	Anilino

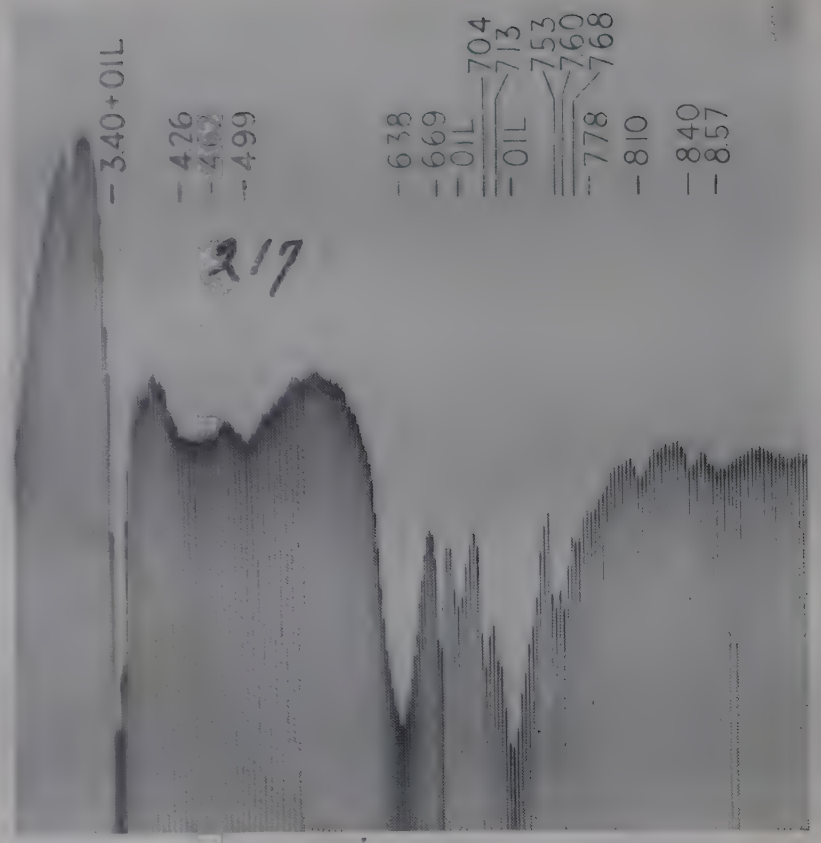
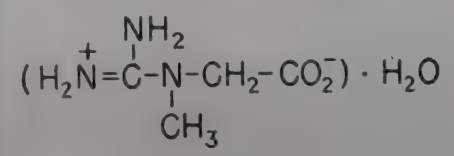


PLATE 62. Assignments: 6.38 μ Carboxylate ion
Preparation: Oil paste

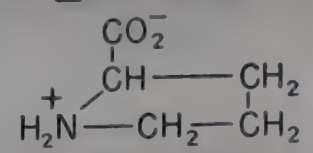
C_6H_5-NH-CH_2-CO_2H
(Top Left and Right)

CREATINE HYDRATE



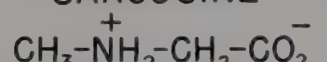
(Bottom Left)

L-PROLINE



(Bottom Center)

SARCOSINE



(Bottom Right)

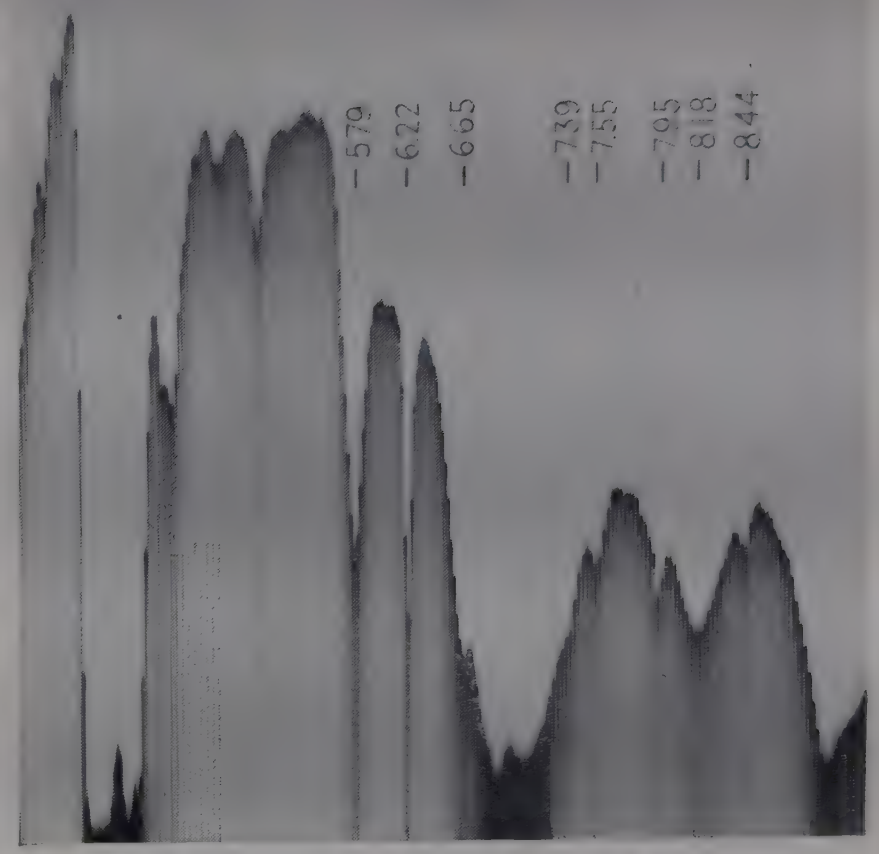


PLATE 62a. Assignments: 6.22 μ, 6.65 μ Phenyl
5.79 μ Acid C=O
Bands not measured—methanol
Preparation: Methanol solution, 0.02 mm.

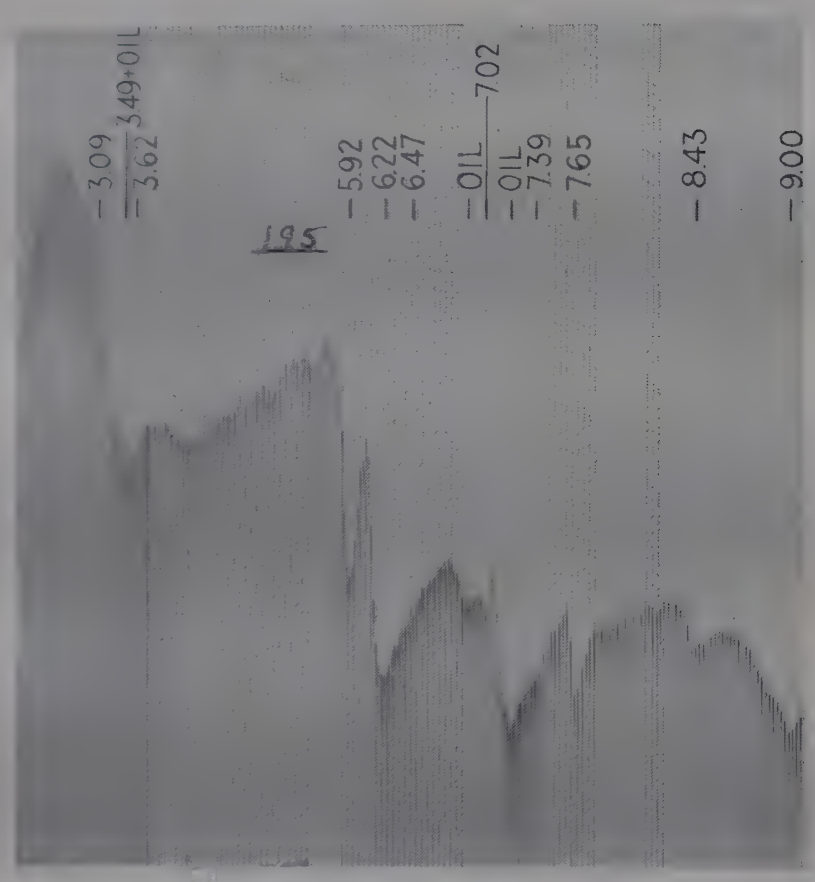


PLATE 63. Preparation: Oil paste

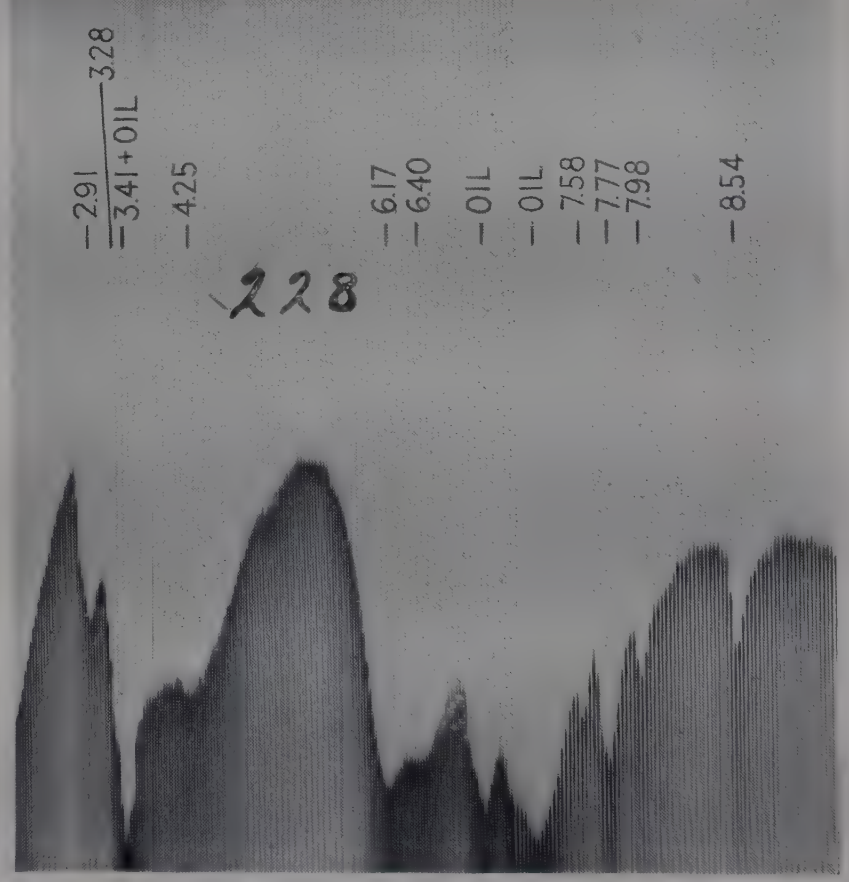


PLATE 64. Assignments: 6.17 μ Carboxylate ion
Oil paste 6.40 μ Unassigned

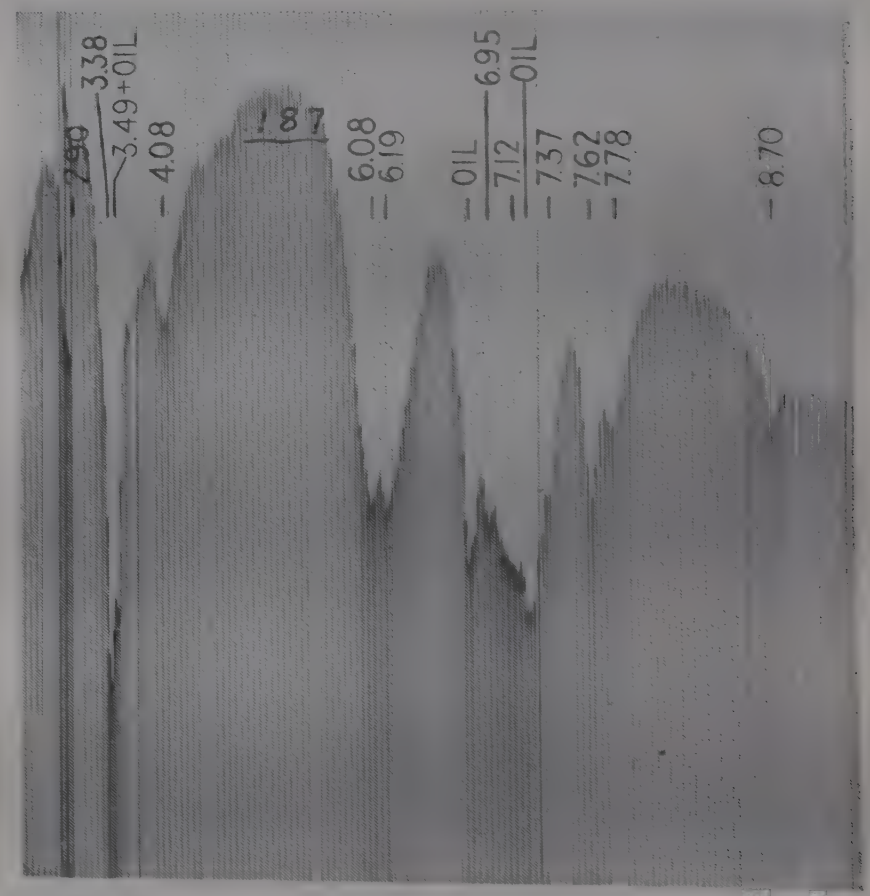


PLATE 65. Assignments: 6.08 μ Unassigned
Oil paste 6.19 μ Carboxylate ion

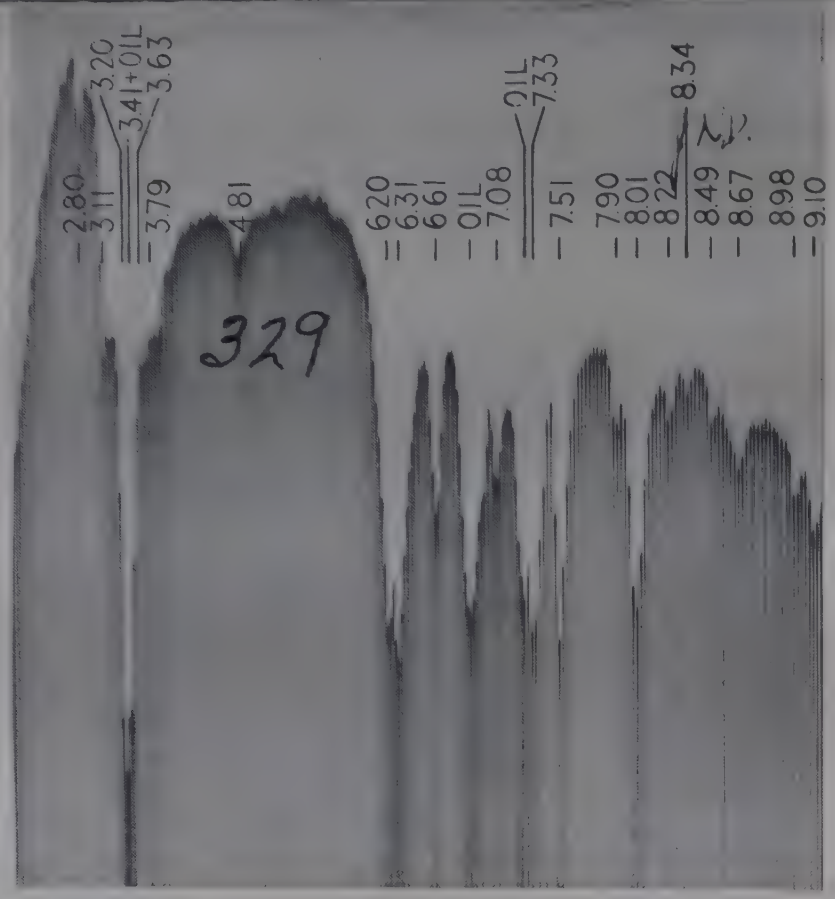
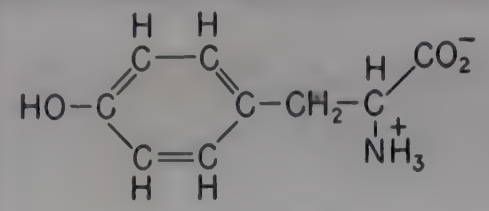


PLATE 66. Assignments: 6.20 μ δNH_3^+, phenyl
6.31 μ Carboxylate ion
6.61 μ Phenyl
Preparation: Oil paste

L-TYROSINE



(Top Left)

dl-β-PHENYLALANINE

$C_6H_5-CH_2-CH(NH_3^+)-CO_2^-$

(Bottom Left)

β-ALANINE

$H_3N^+-CH_2-CH_2-CO_2^-$

(Top Right)

d-GLUTAMIC ACID

$HO_2C-(CH_2)_2-CH(NH_3^+)-CO_2^-$

(Bottom Center)

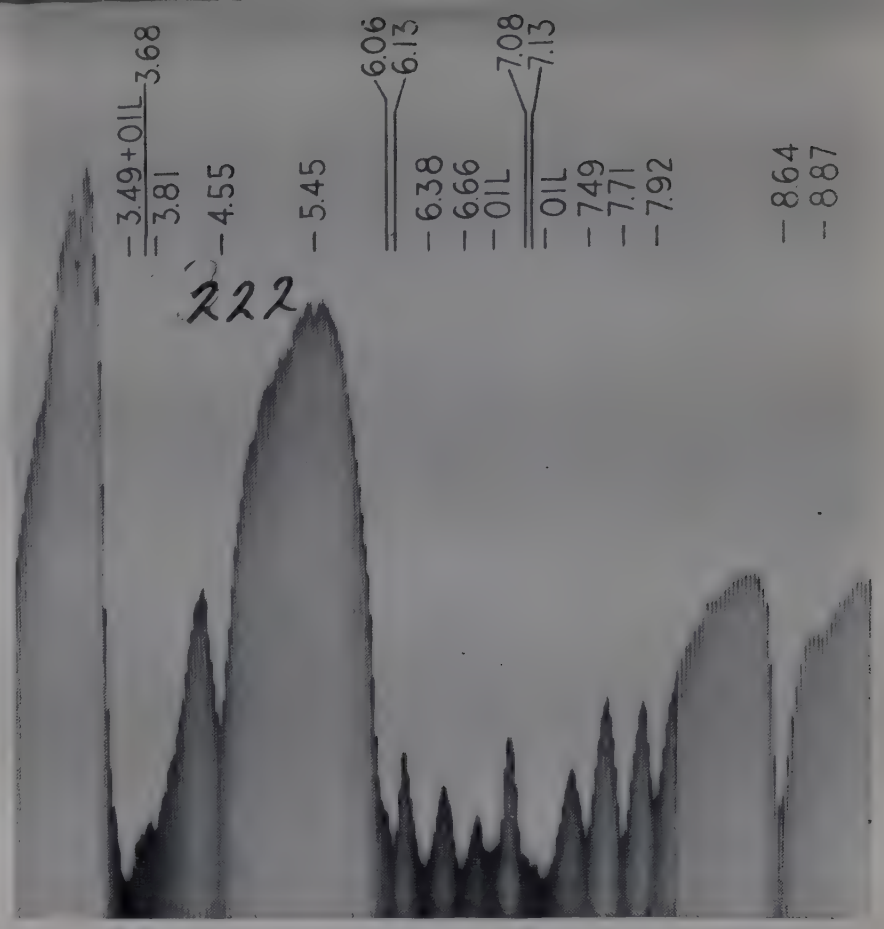


PLATE 67. Assignments: 6.06 μ Unassigned
6.13 μ Amino acid I (δNH_3^+)
6.38 μ Carboxylate ion
6.66 μ Amino acid II
Preparation: Oil paste

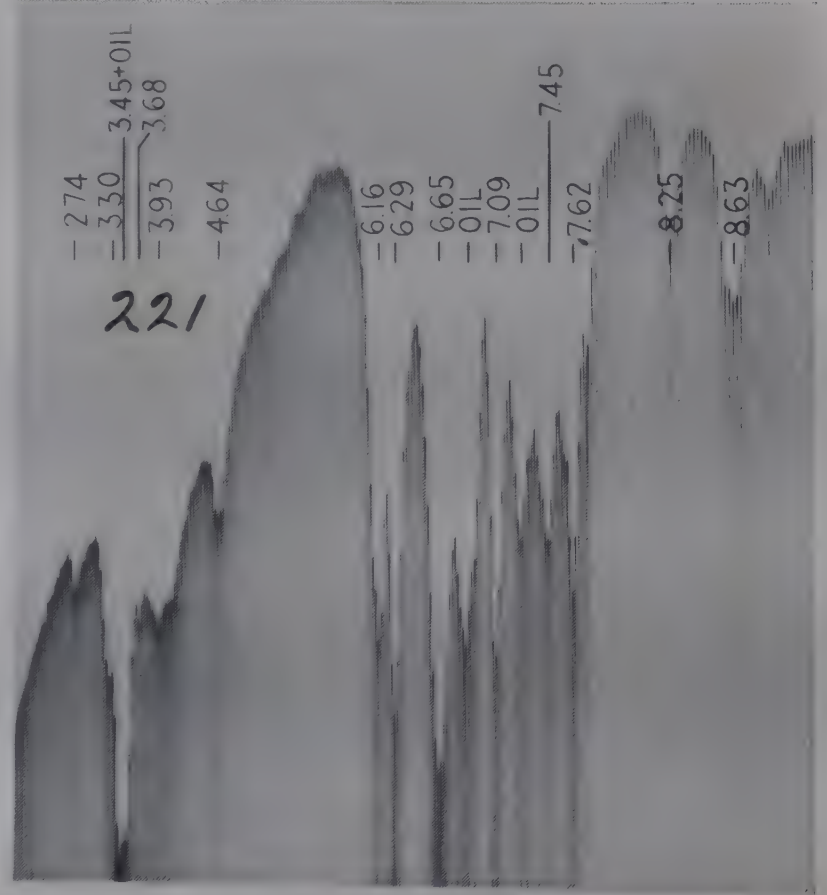


PLATE 68. Assignments: 6.16 μ Amino acid I (δNH_3^+)
6.29 μ Carboxylate ion
6.65 μ Amino acid II

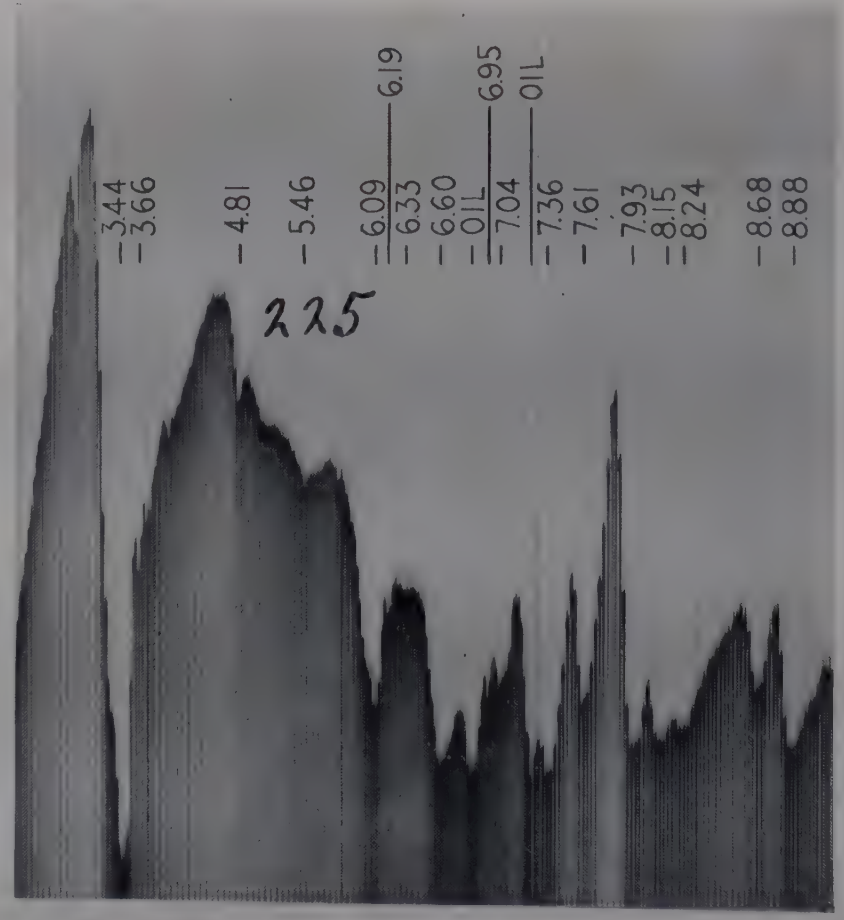


PLATE 69. Assignments:
6.09 μ Carboxylate ion, δNH_3^+

ACETYL BROMIDE

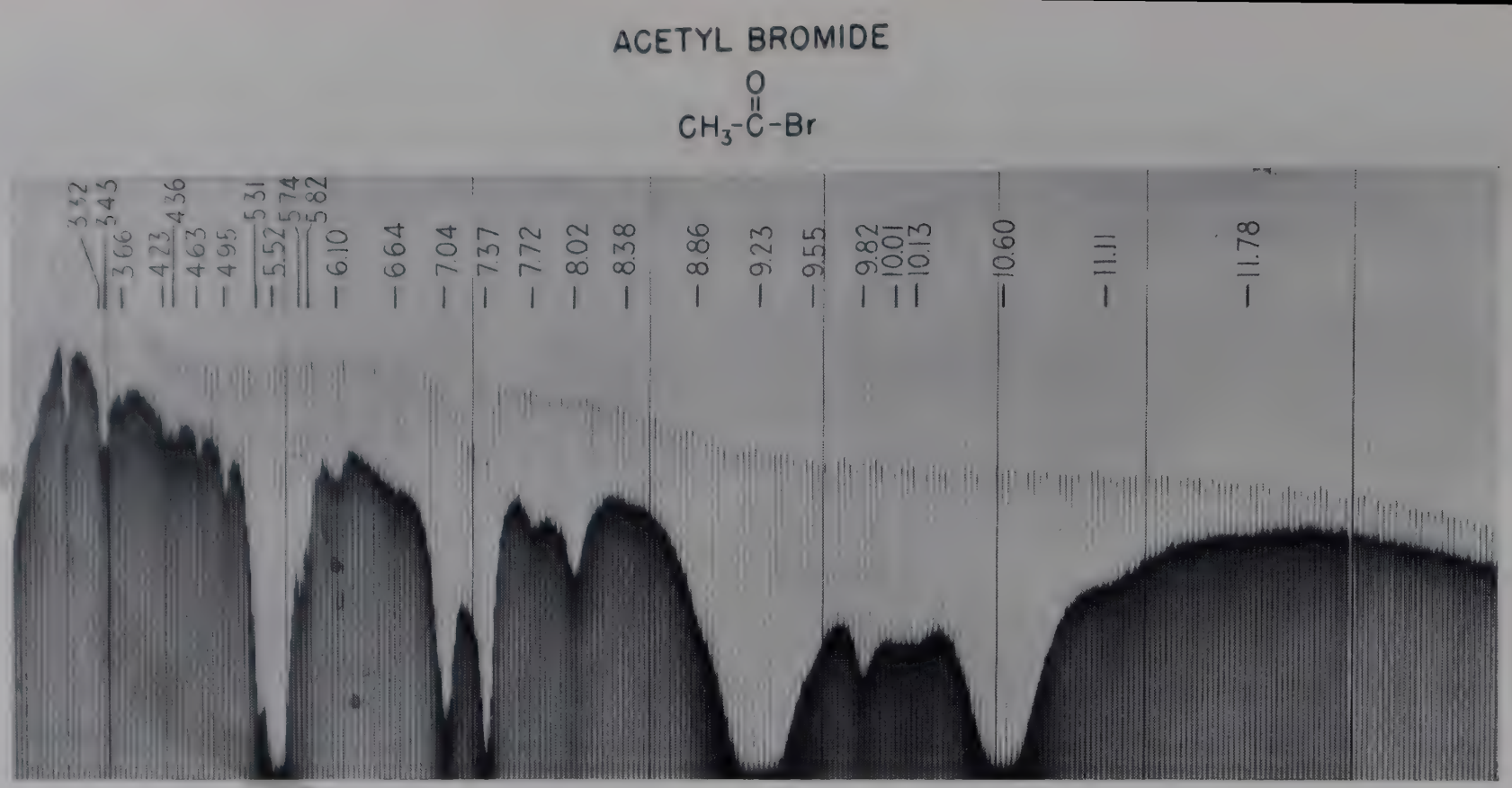


PLATE 70. Assignments: 5.52 μ C=O Preparation: 0.15 mm.

ACETYL CHLORIDE

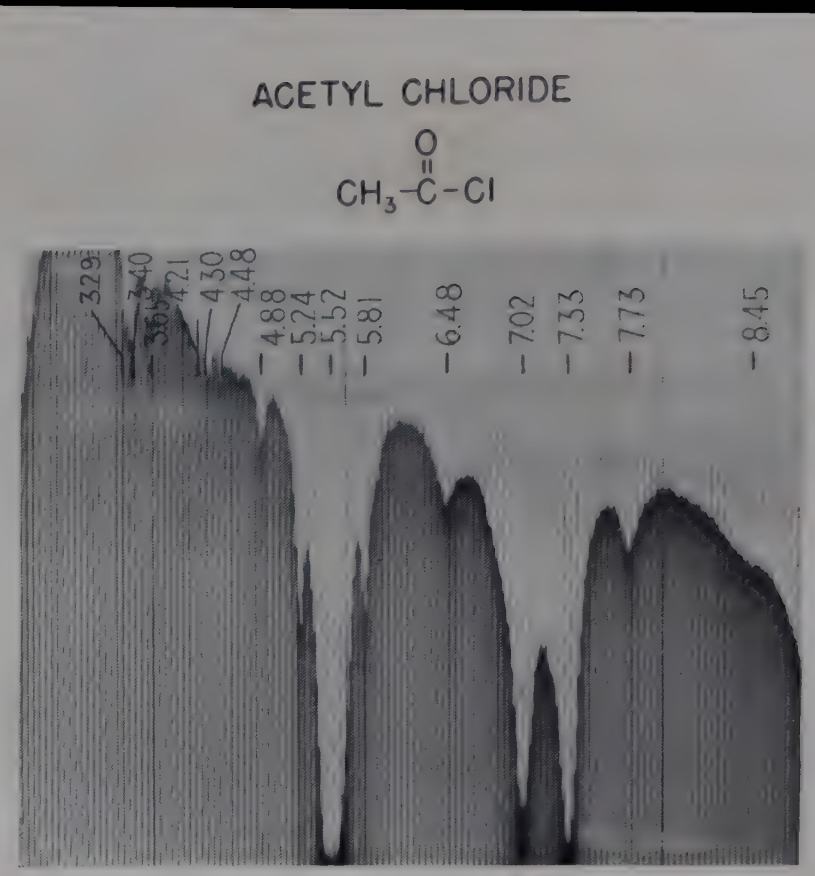


PLATE 71. Assignments: 5.52 μ C=O
Preparation: Deposited from chloroform

BENZOYL CHLORIDE

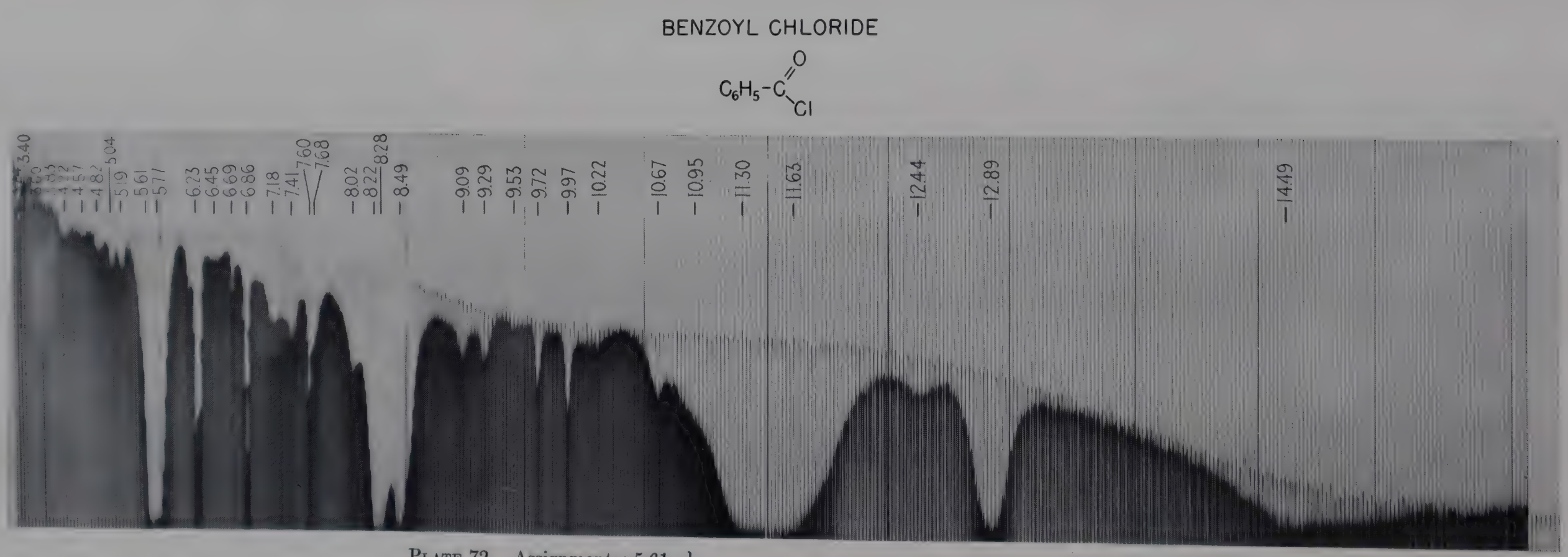


PLATE 72. Assignments: 5.61 μ, 5.77 μ } C=O
6.23 μ, 6.69 μ } Conjugated phenyl
Preparation: 0.015 mm.

ACETAMIDE

$$CH_3-C(=O)-NH_2$$

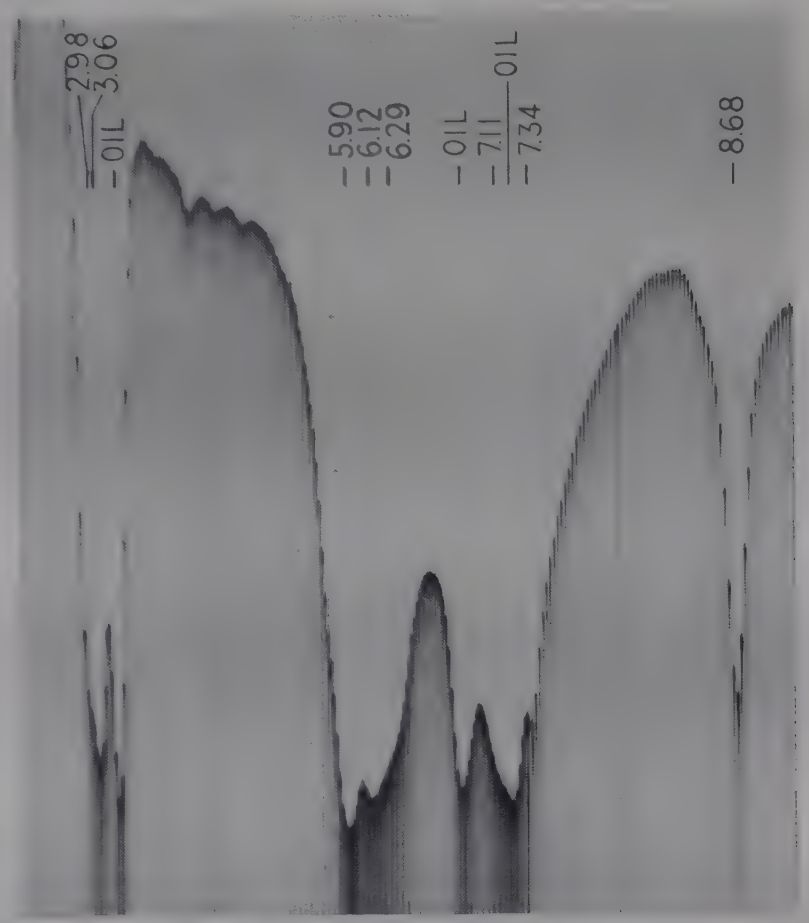


PLATE 74. Assignments: 5.90 μ Amide C=O
6.12 μ δNH_2
Preparation: Oil paste

PHENACETAMIDE

$$C_6H_5-CH_2-C(=O)-NH_2$$

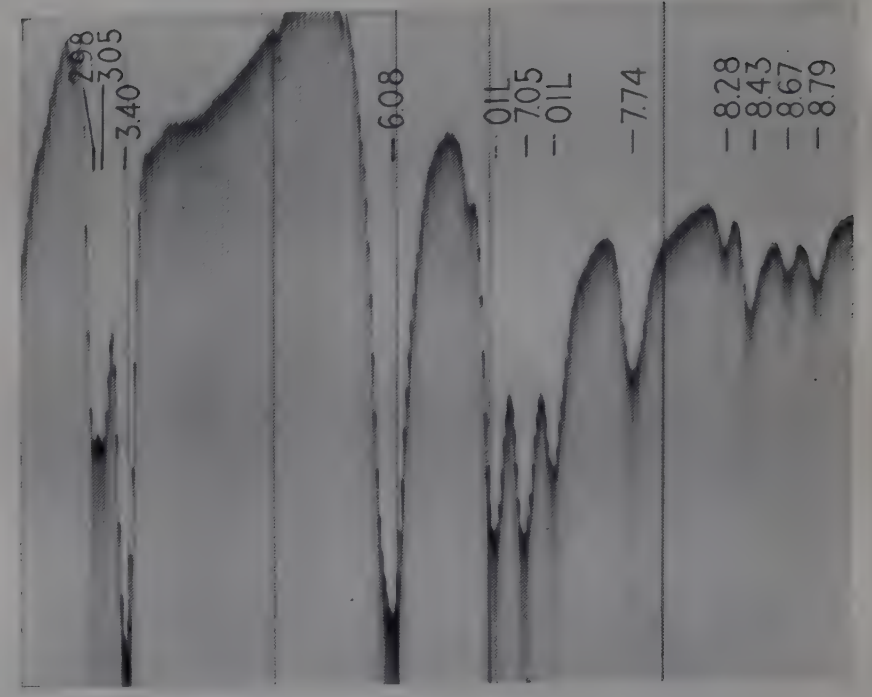


PLATE 75. Assignments: 6.08 μ {Amide C=O / δNH_2
Preparation: Oil paste

PHENACETYL CHLORIDE

$$C_6H_5-CH_2-C(=O)-Cl$$

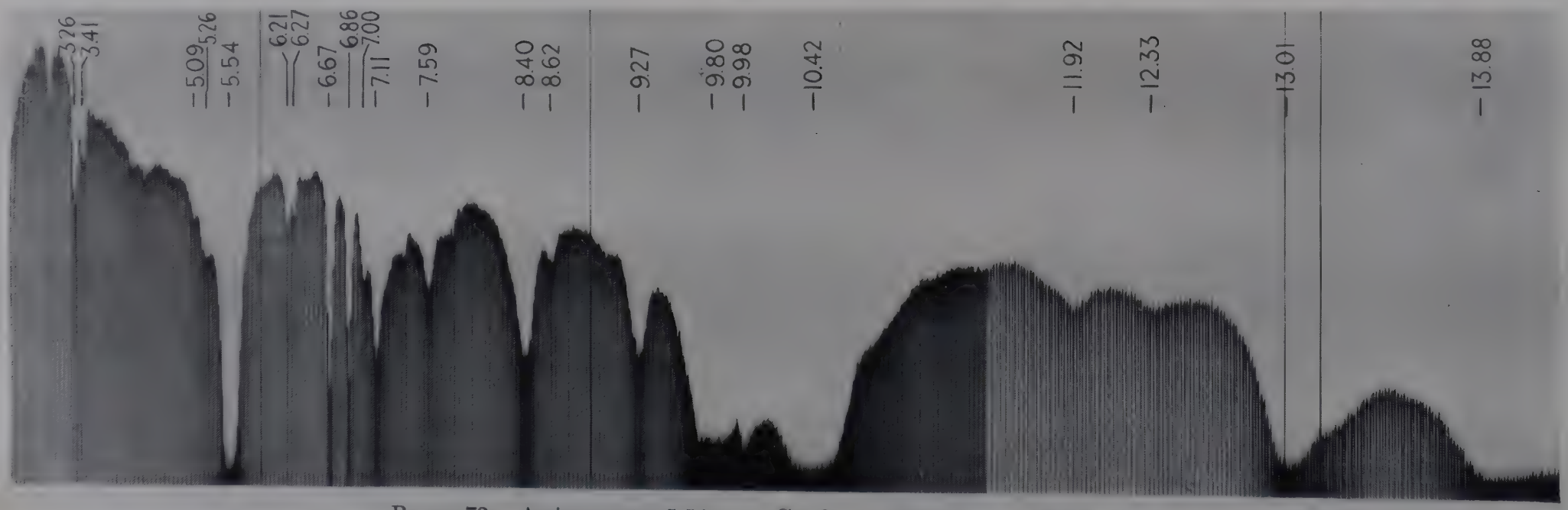


PLATE 73. Assignments: 5.54 μ C=O
6.21 μ / 6.67 μ Phenyl
Preparation: 0.015 mm.

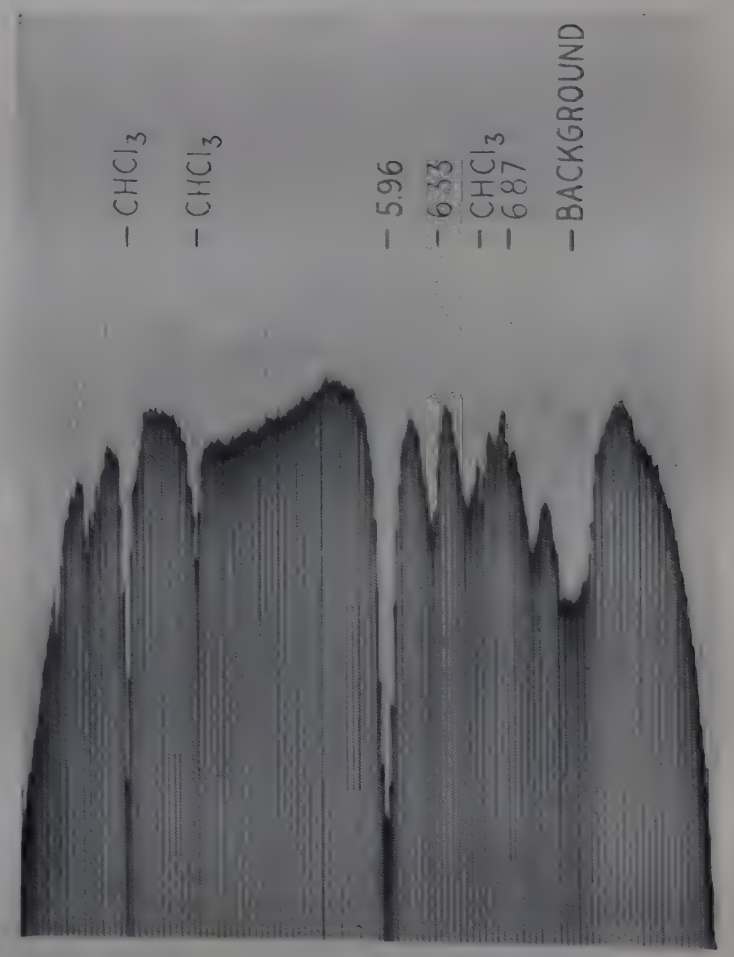


PLATE 75a. Assignments:
5.96 μ Amide C=O
Preparation: 2% solution in

BENZAMIDE

$C_6H_5-CO-NH_2$

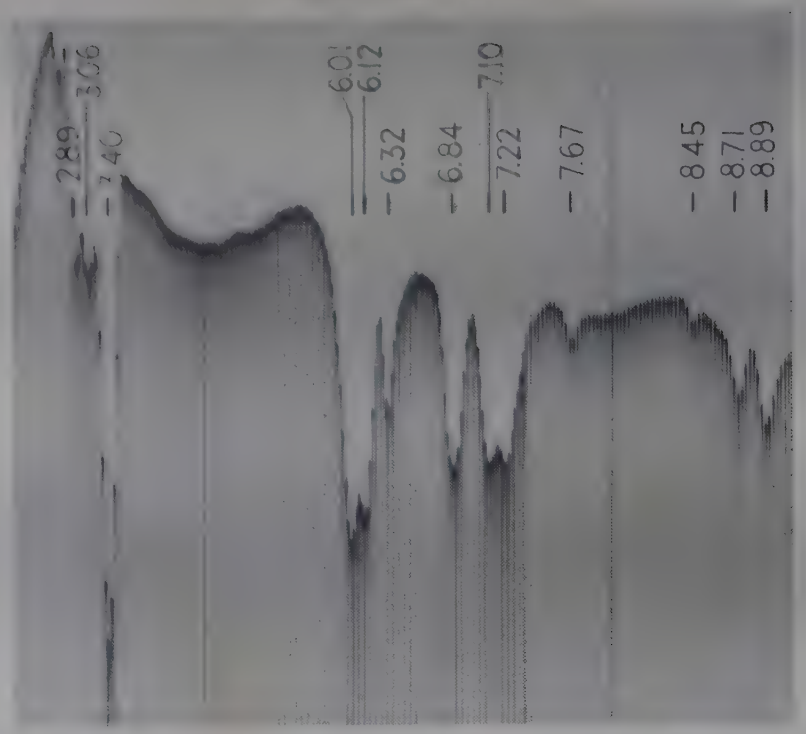
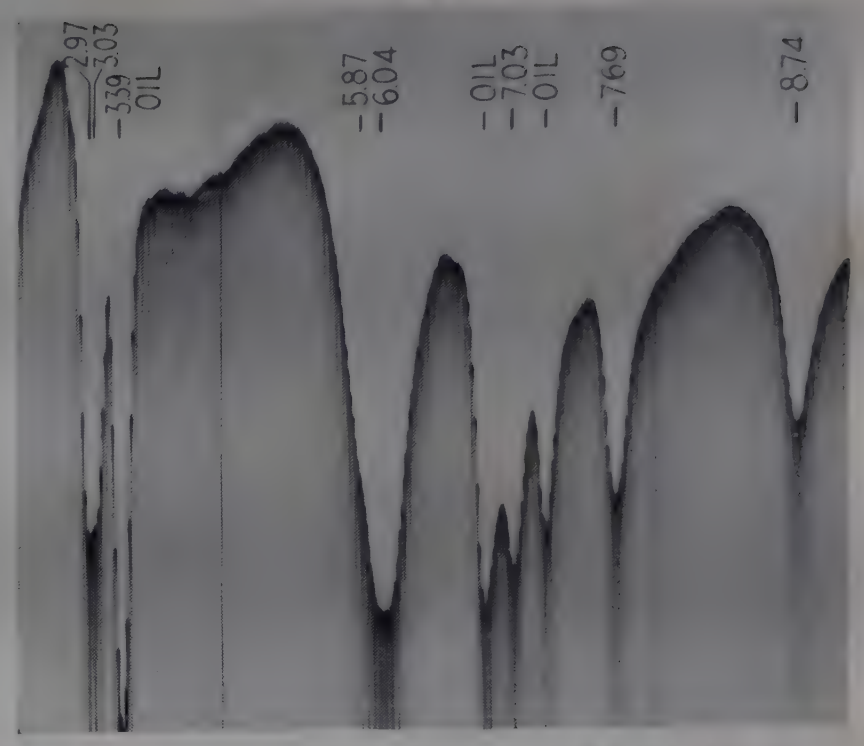


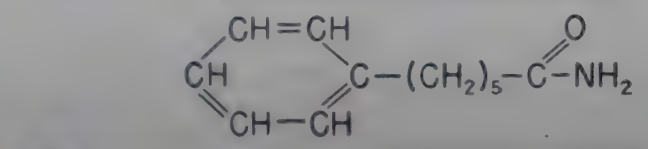
PLATE 76. Assignments: 6.01 μ Amide C=O
6.12 μ δNH_2
6.32 μ Phenyl
Preparation: Oil paste



$CH_3 \cdot CH_2 \cdot C(=O)-NH_2$

PLATE 77. Assignments: 6.04 μ { Amide C=O, δNH_2
Preparation: Oil paste

ϵ-PHENYLCAPROAMIDE



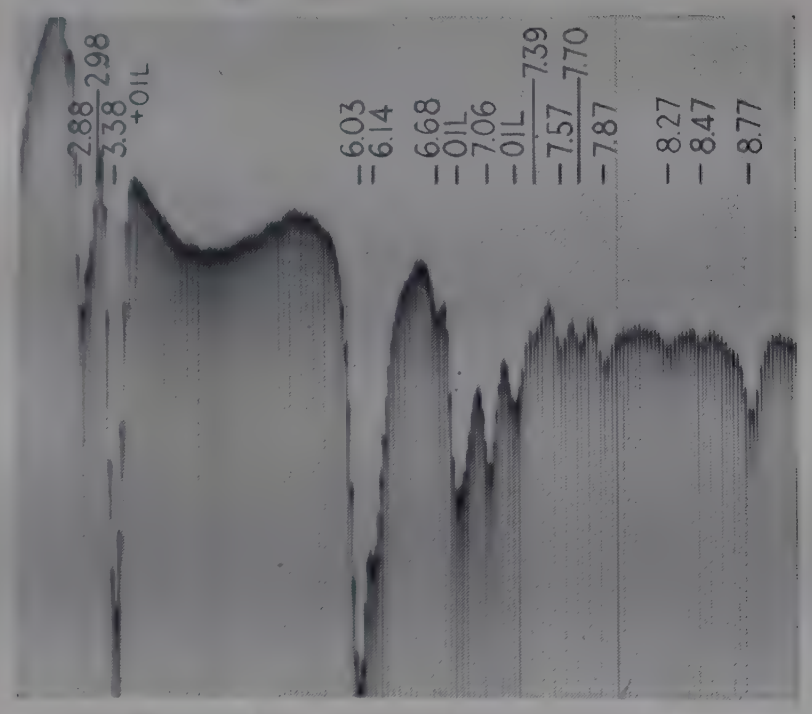


PLATE 78. Assignments: 6.03 μ Amide C=O
6.14 μ δNH_2
Preparation: Oil paste

MALONAMIDE

$H_2N-C(=O)-CH_2-C(=O)-NH_2$

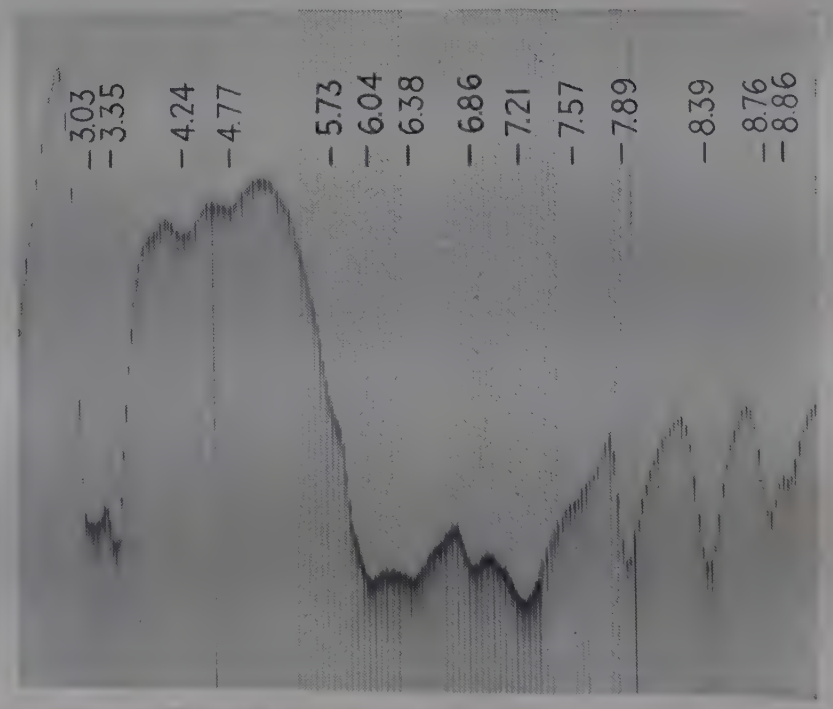


PLATE 79. Preparation: Oil paste

CYANOACETAMIDE

$N\equiv C-CH_2-C(=O)-NH_2$

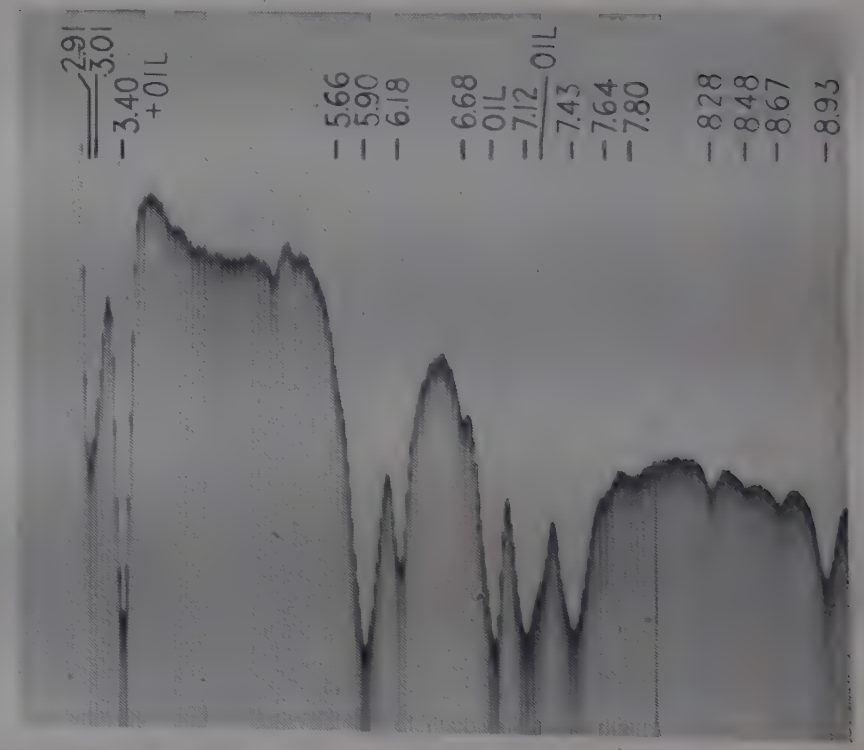
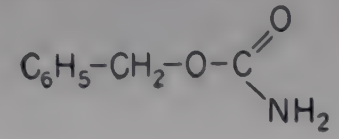


PLATE 80. Assignments: 5.90 μ Amide C=O
6.18 μ δNH_2
Preparation: Oil paste

BENZYL CARBAMATE



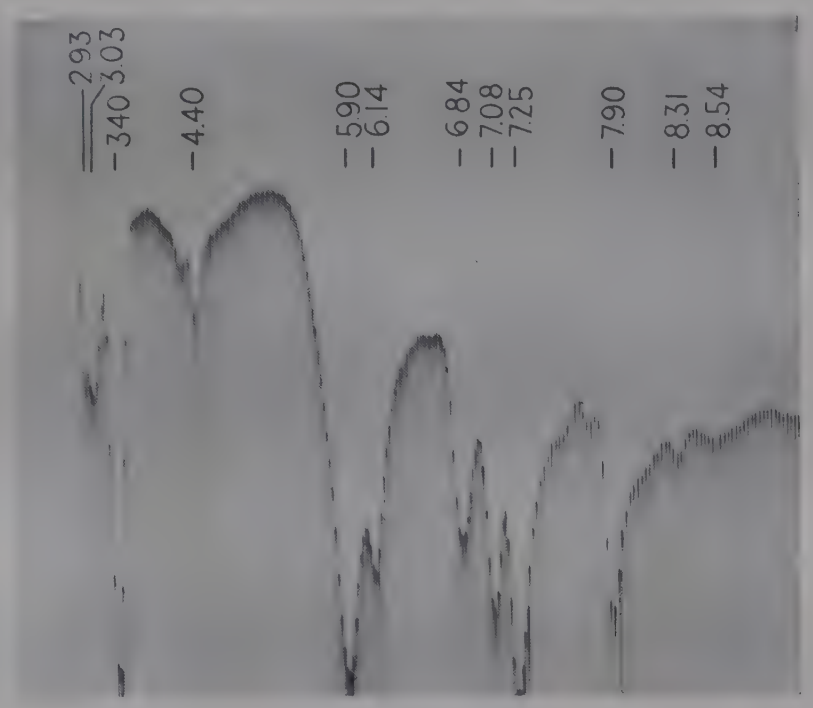
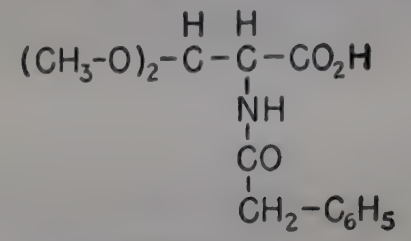


PLATE 81. Assignments: 5.90 μ {Acid C=O / Amide C=O; 6.14 μ NH_2
Preparation: Oil paste

α-PHENACETAMIDO-β,β-DIMETHOXY PROPIONIC ACID



(Top Right)

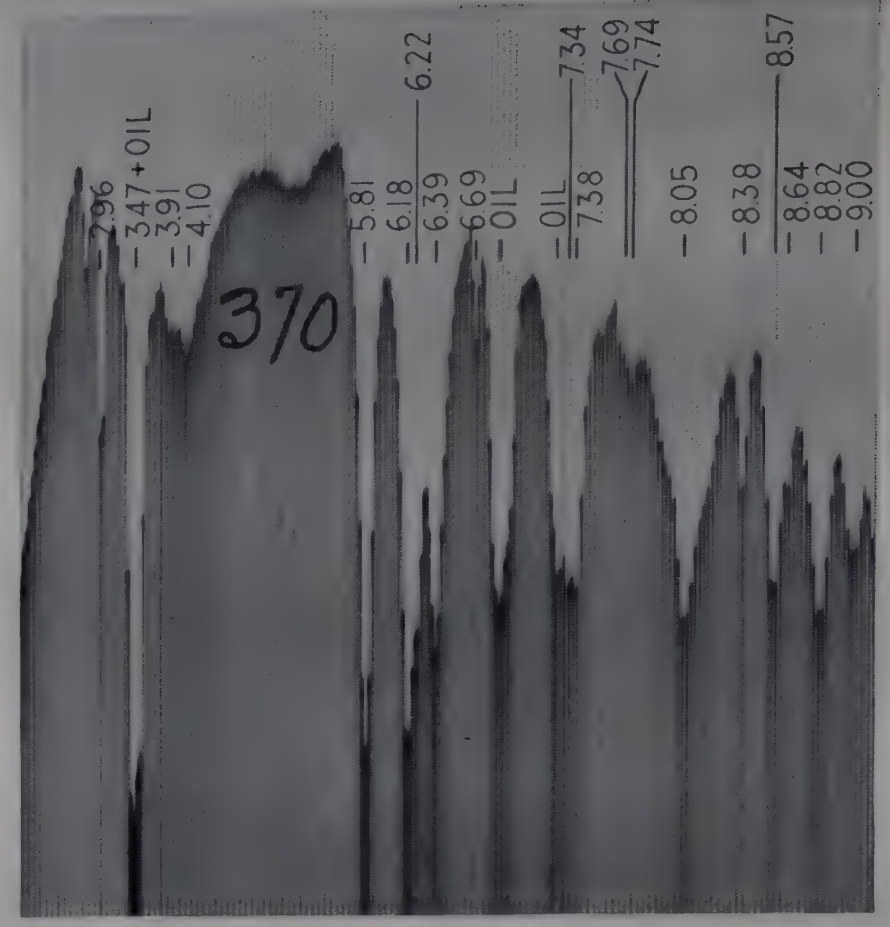
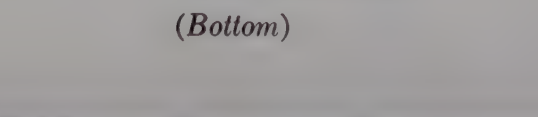


PLATE 84. 5.81 μ Acid C=O; 6.18 μ Amide I; 6.39 μ Amide II; 6.22 μ, 6.69 μ Phenyl. Oil paste

α-ACETAMIDO-β,β-DIMETHYLACRYLIC ACID



(Bottom)

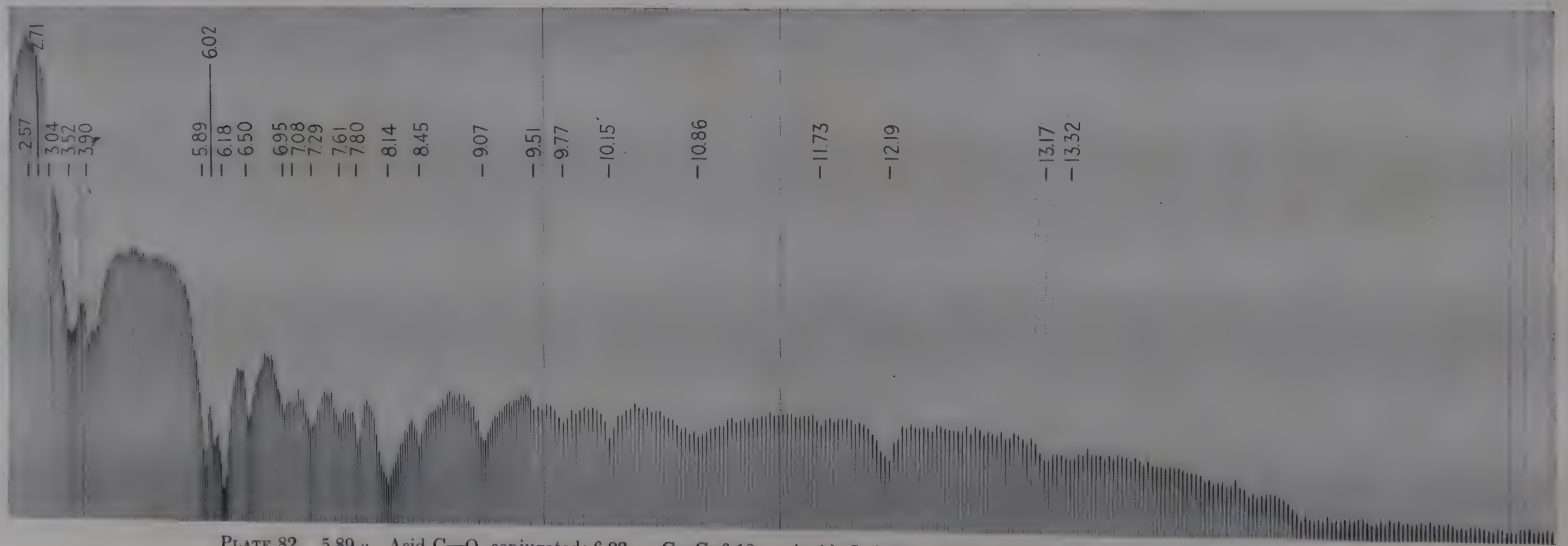


PLATE 82. 5.89 μ Acid C=O, conjugated; 6.02 μ C=C; 6.18 μ Amide I; 6.50 μ Amide II. Deposited from tetrachloroethane

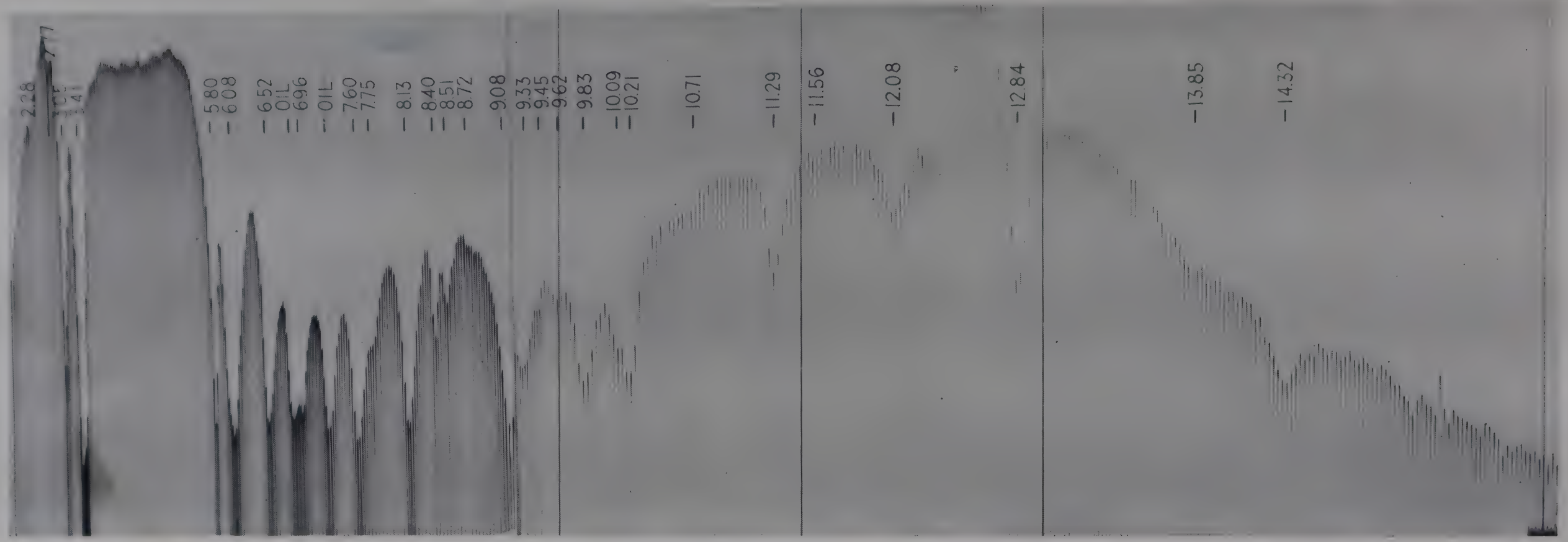


PLATE 83. 5.80 μ Conj. ester C=O; 6.08 μ Amide I plus C=C; 6.52 μ Amide II. 2.0–9.0 μ (oil paste); 9.0–15 μ dep. from $CHCl_3$

α-PHENACETAMIDO-β, β-DIMETHOXY
PROPIONIC ACID METHYL ESTER

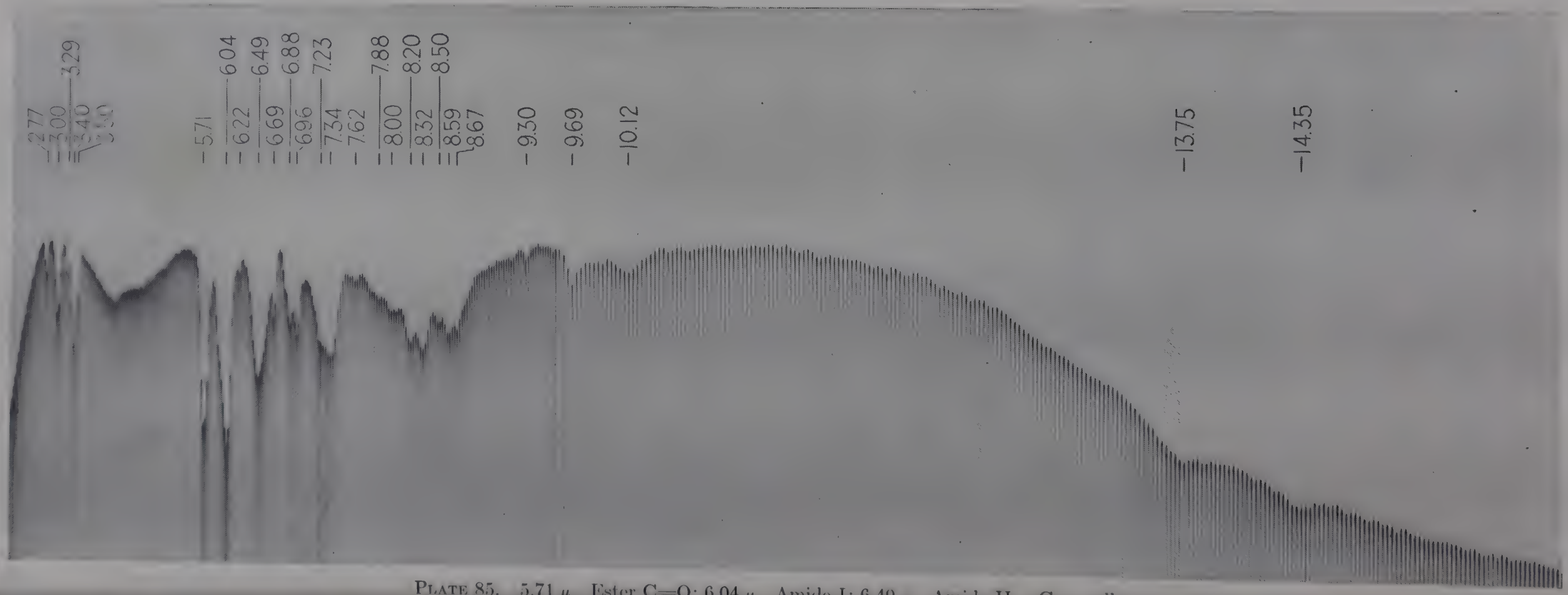
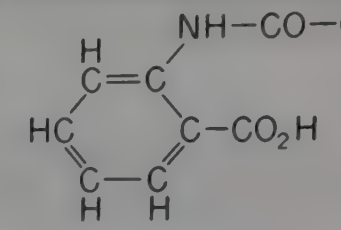


PLATE 85. 5.71 μ Ester C=O; 6.04 μ Amide I; 6.49 μ Amide II. Cap. cell

N-PHENACETYLANTHRANILIC ACID



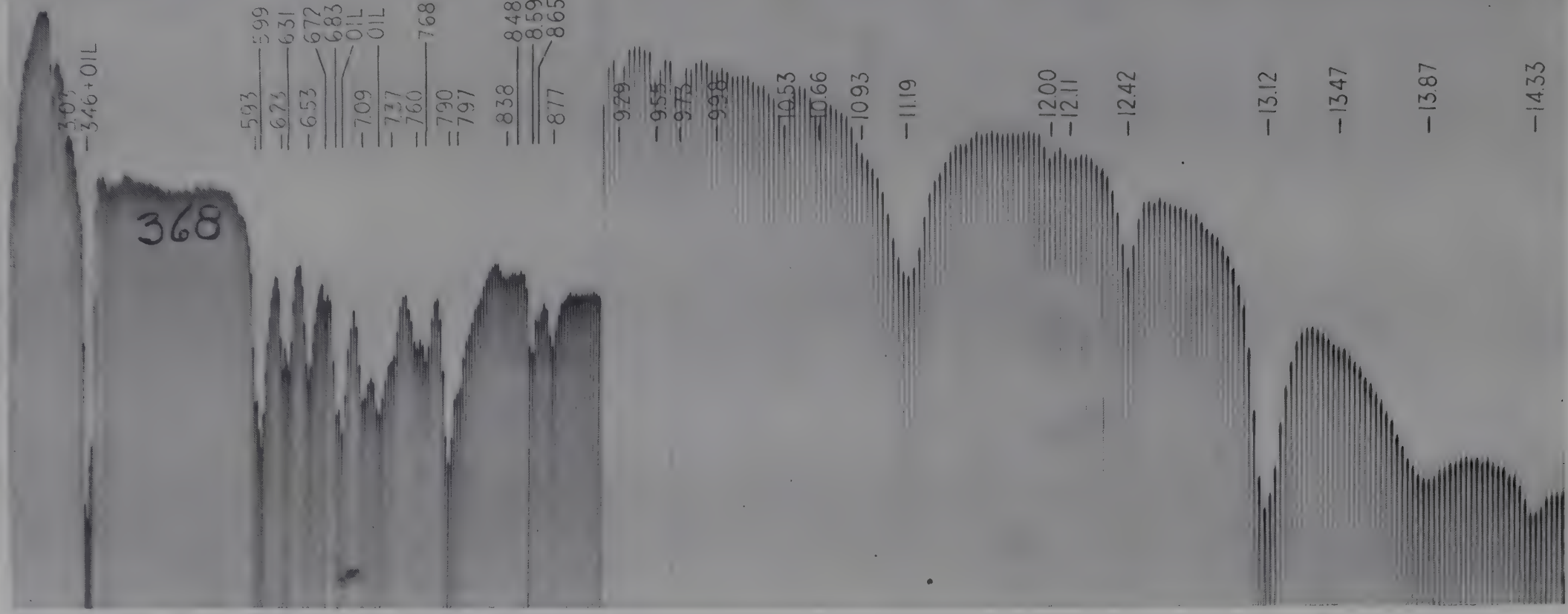


PLATE 86. 5.93 μ Conj. acid C=O; 5.99 μ Amide I; 6.53 μ Amide II; 6.23 μ, 6.31 μ, 6.72 μ Conj. phenyl. Oil paste

N-PHENACETYLANTHRANILIC ACID
METHYL ESTER

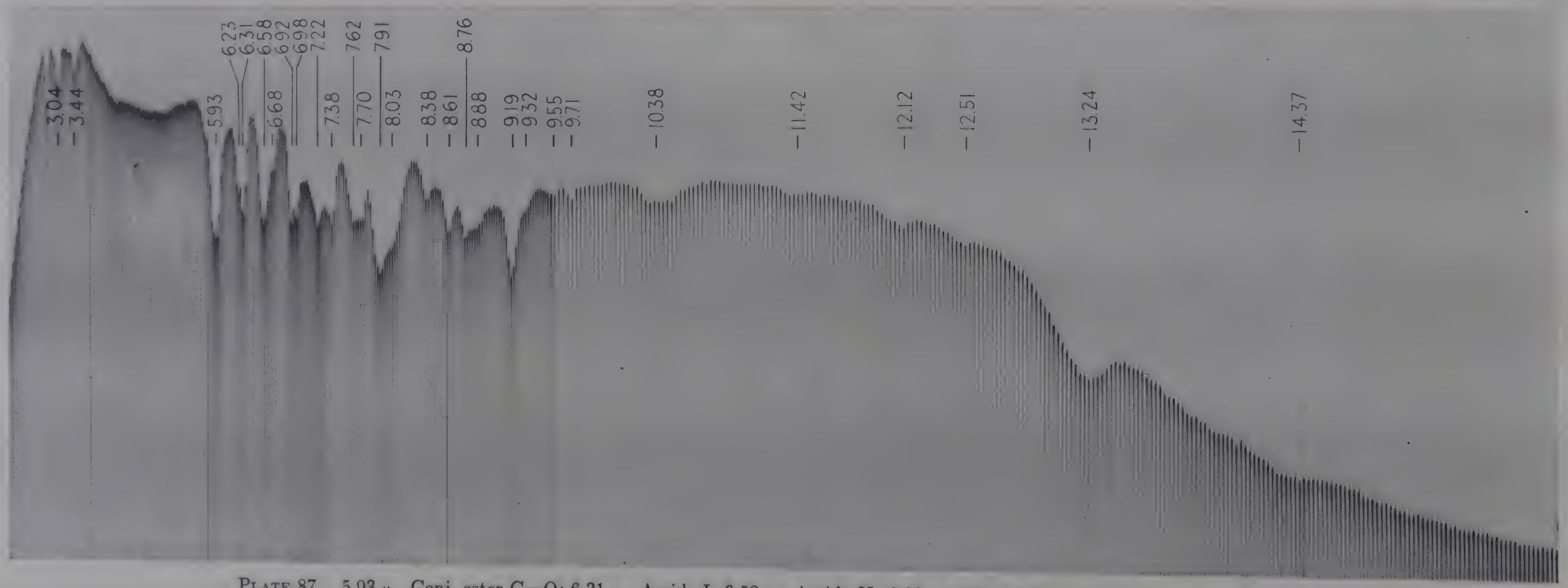
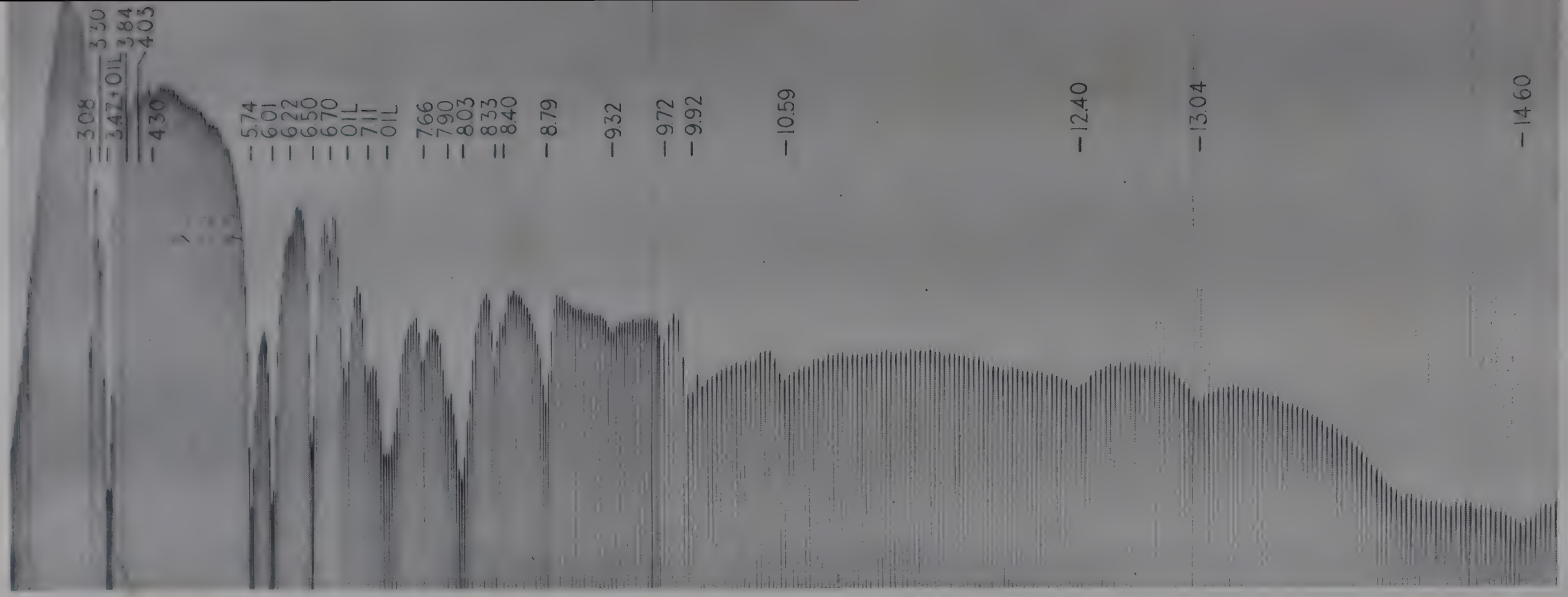


PLATE 87. 5.93 μ Conj. ester C=O; 6.31 μ Amide I; 6.58 μ Amide II; 6.23 μ, 6.31 μ, 6.68 μ Conj. phenyl. Cap. cell



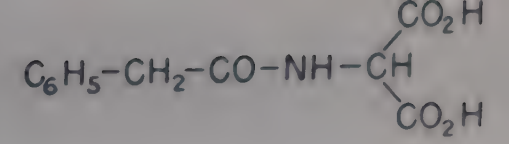


PLATE 88. Assignments: 5.74 μ Acid C=O Preparation: Oil paste
6.01 μ Amide I
6.50 μ Amide II

PHENACETAMIDOMALONIC ACID MONOETHYL ESTER

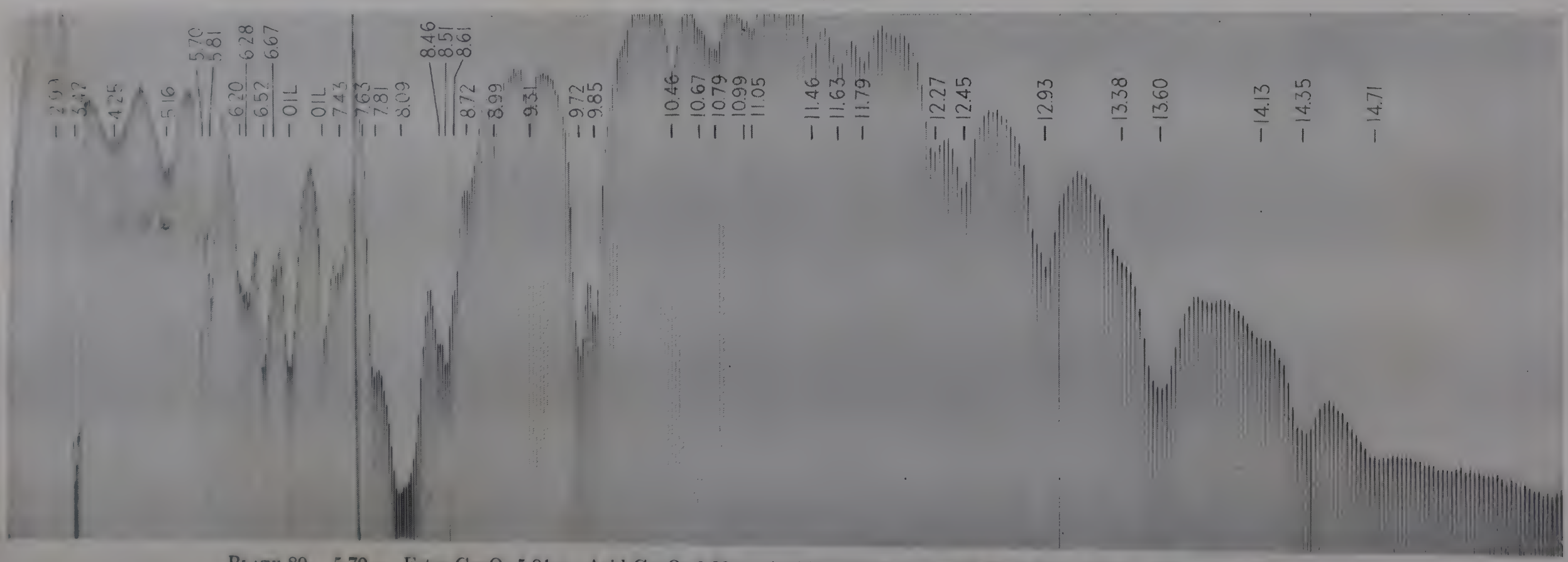
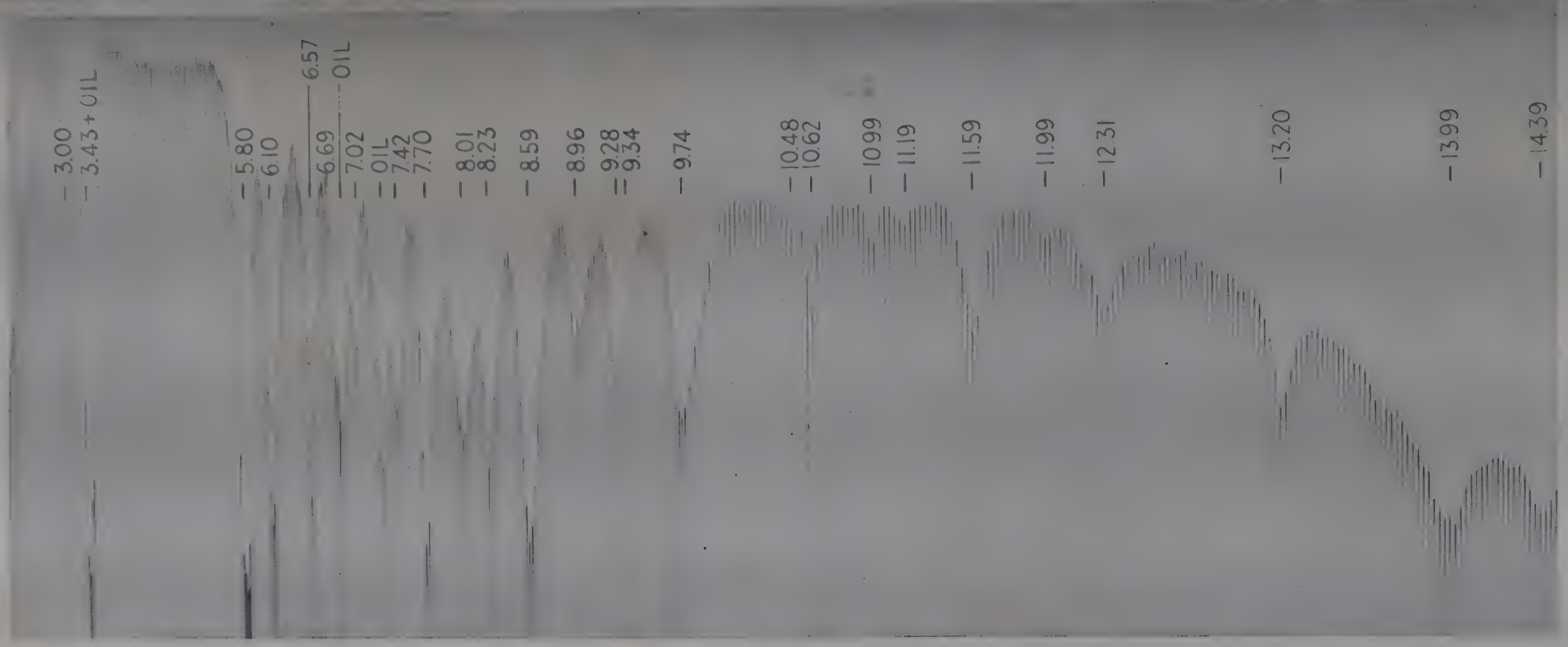


PLATE 89. 5.70 μ Ester C=O; 5.81 μ Acid C=O; 6.20 μ Amide I; 6.52 μ Amide II; 6.28 μ, 6.67 μ Phenyl. Oil paste



PHENACETAMIDOSUCCINIC ACID DIETHYL ESTER

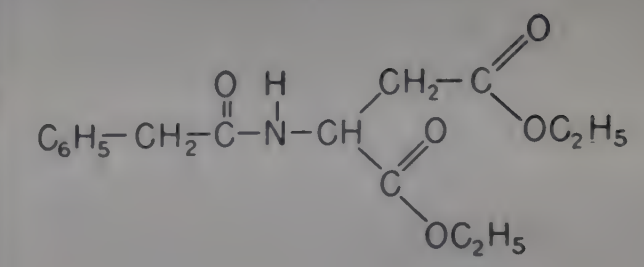
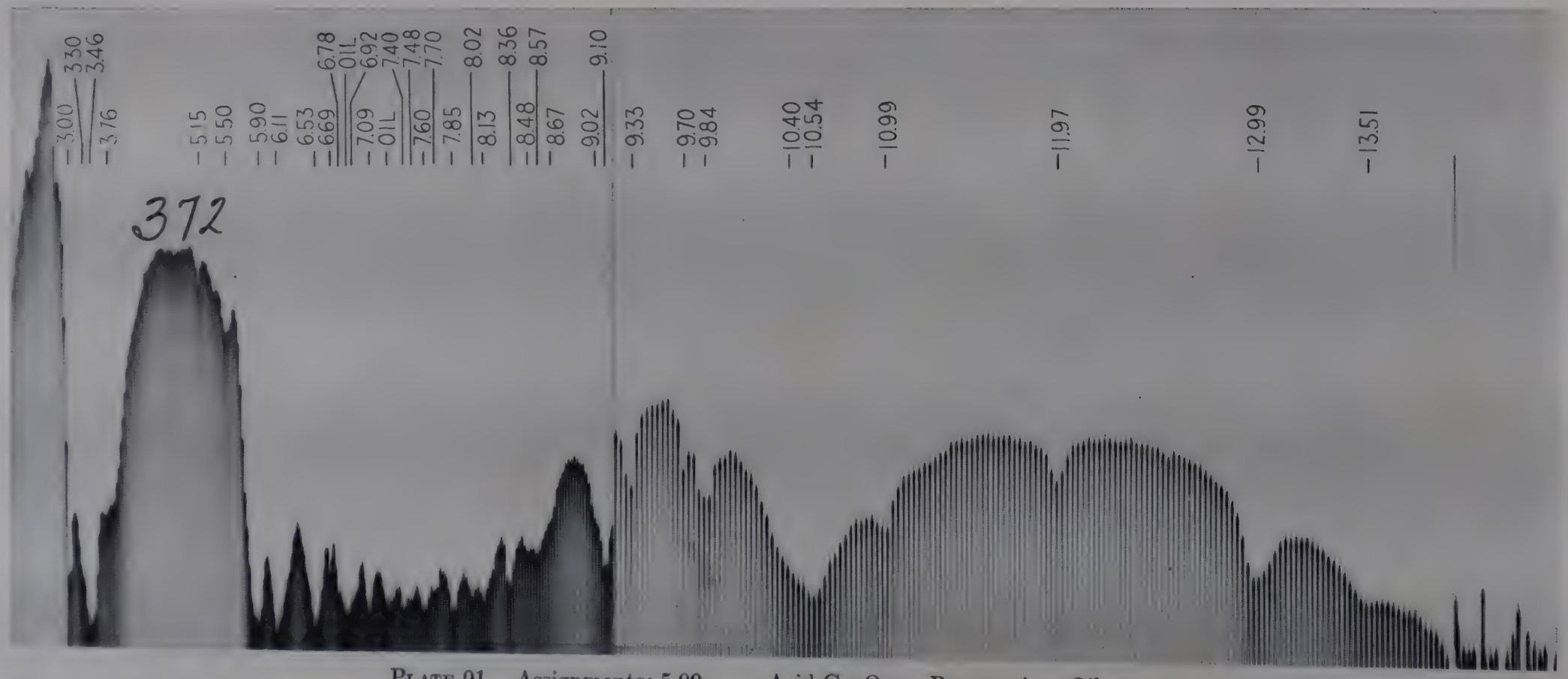


PLATE 90. Assignments: 5.80 μ Ester C=O Preparation: Oil paste
6.10 μ Amide I
6.57 μ Amide II



ϵ-PHENACETAMIDO-n-CAPROIC ACID

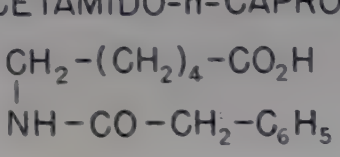


PLATE 91. Assignments: 5.90 μ Acid C=O Preparation: Oil paste
6.11 μ Amide I
6.53 μ Amide II

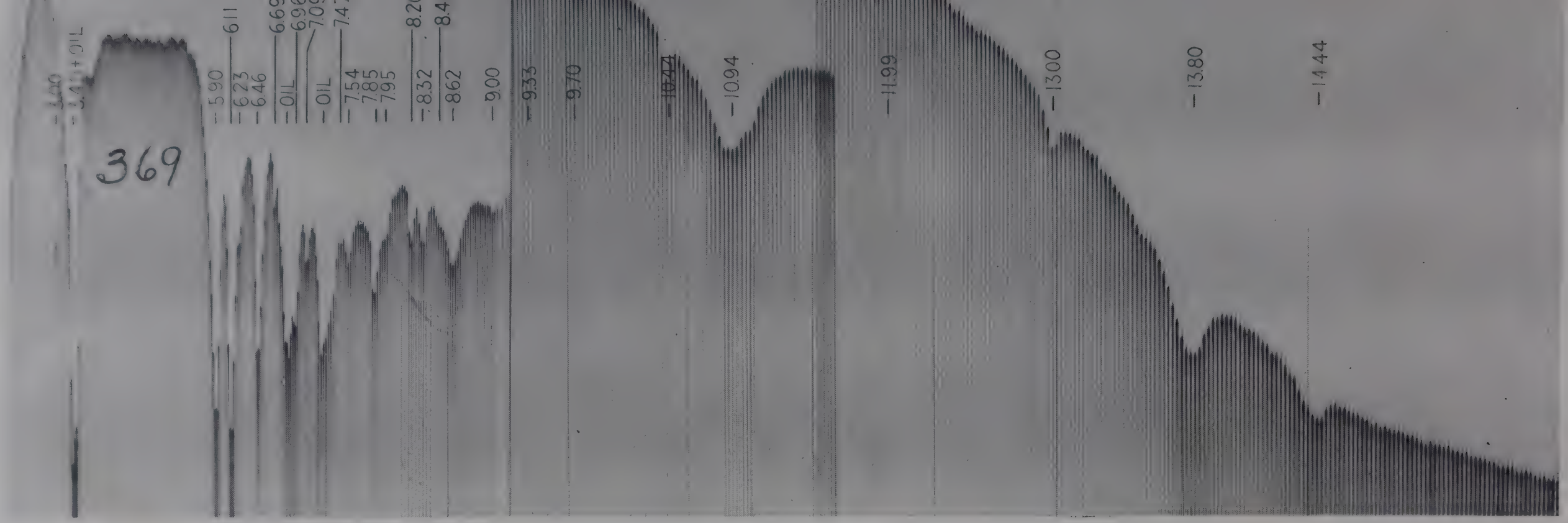


PLATE 92. Assignments: 5.90 μ Acid C=O; 6.11 μ Amide I; 6.46 μ Amide II; 6.23 μ, 6.69 μ Phenyl. Preparation: Oil paste

δ-PHENACETAMIDO-n-VALERIC ACID

$CH_2-(CH_2)_3-CO_2H$

$NH-CO-CH_2-C_6H_5$

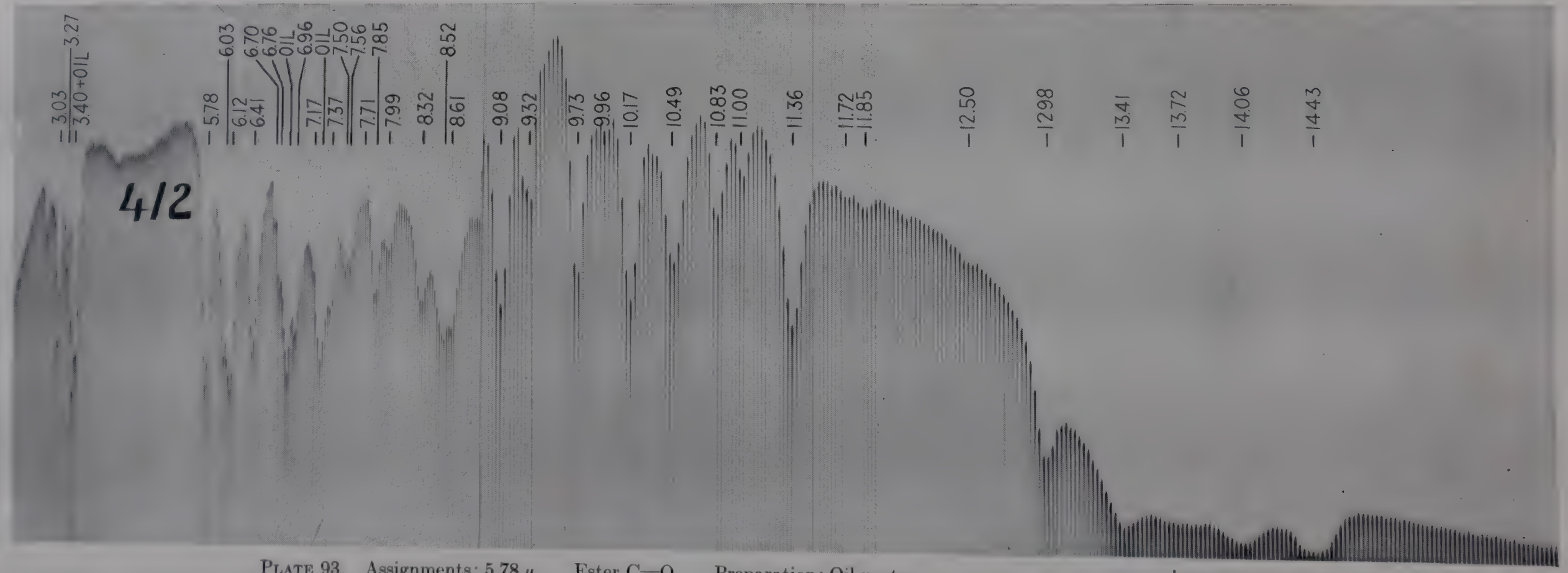
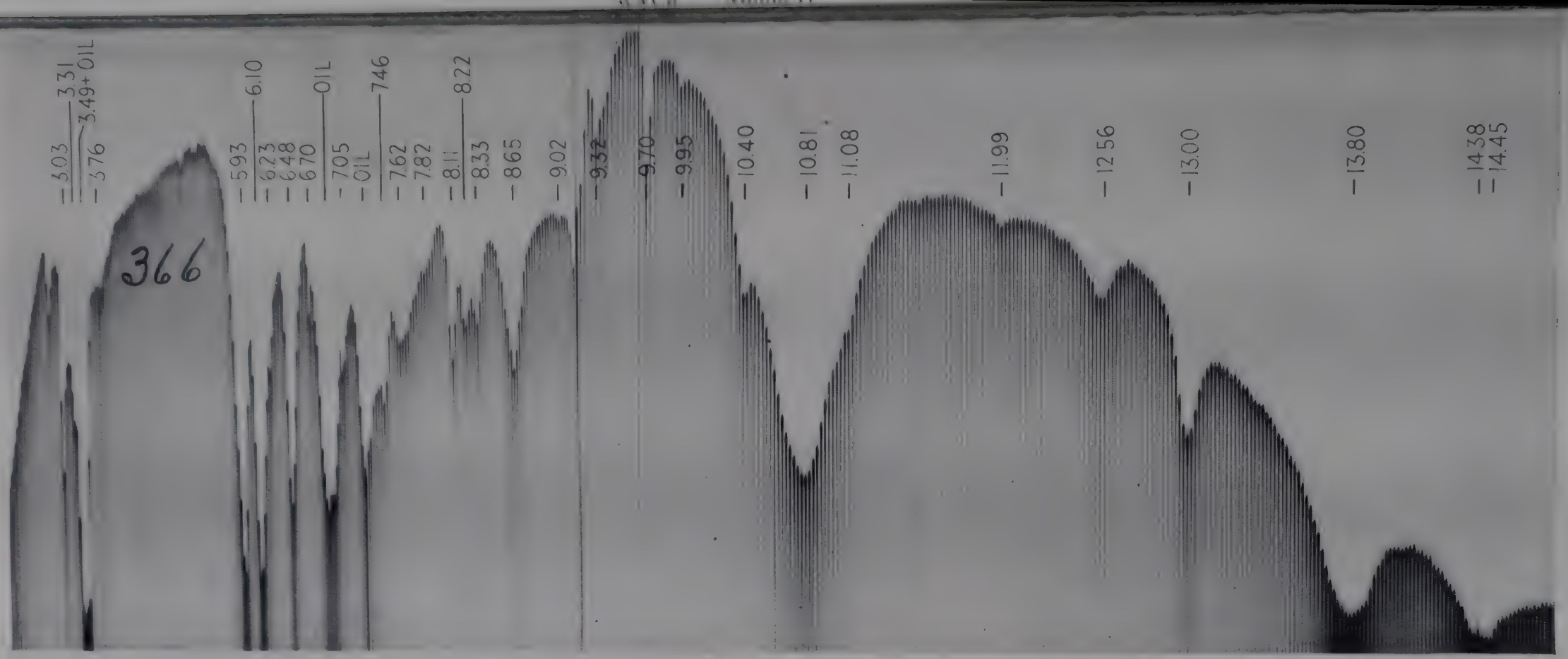


PLATE 93. Assignments: 5.78 μ Ester C=O; 6.12 μ Amide I; 6.41 μ Amide II. Preparation: Oil paste

δ-PHENACETAMIDO-n-VALERIC ACID
METHYL ESTER

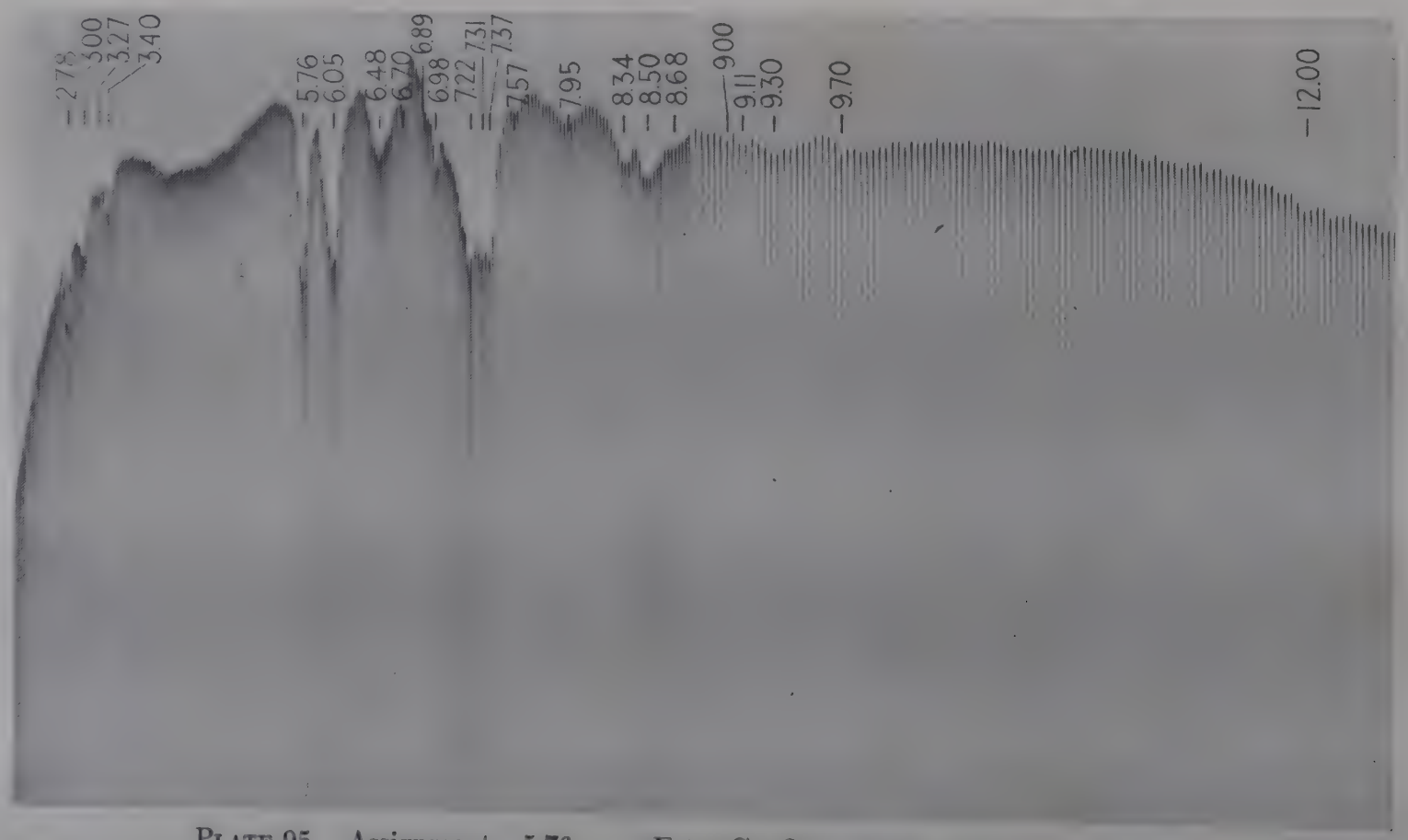


N-PHENACETYL-β-ALANINE

$NH-CH_2-CH_2-CO_2H$

$CO-CH_2-C_6H_5$

PLATE 94. Assignments: 5.93 μ Acid C=O Preparation: Oil paste
6.10 μ Amide I
6.48 μ Amide I
6.23 μ, 6.70 μ Phenyl



N-PHENACETYL-β-ALANINE
METHYL ESTER

PLATE 95. Assignments: 5.76 μ Ester C=O Preparation: Capillary cell
6.05 μ Amide I

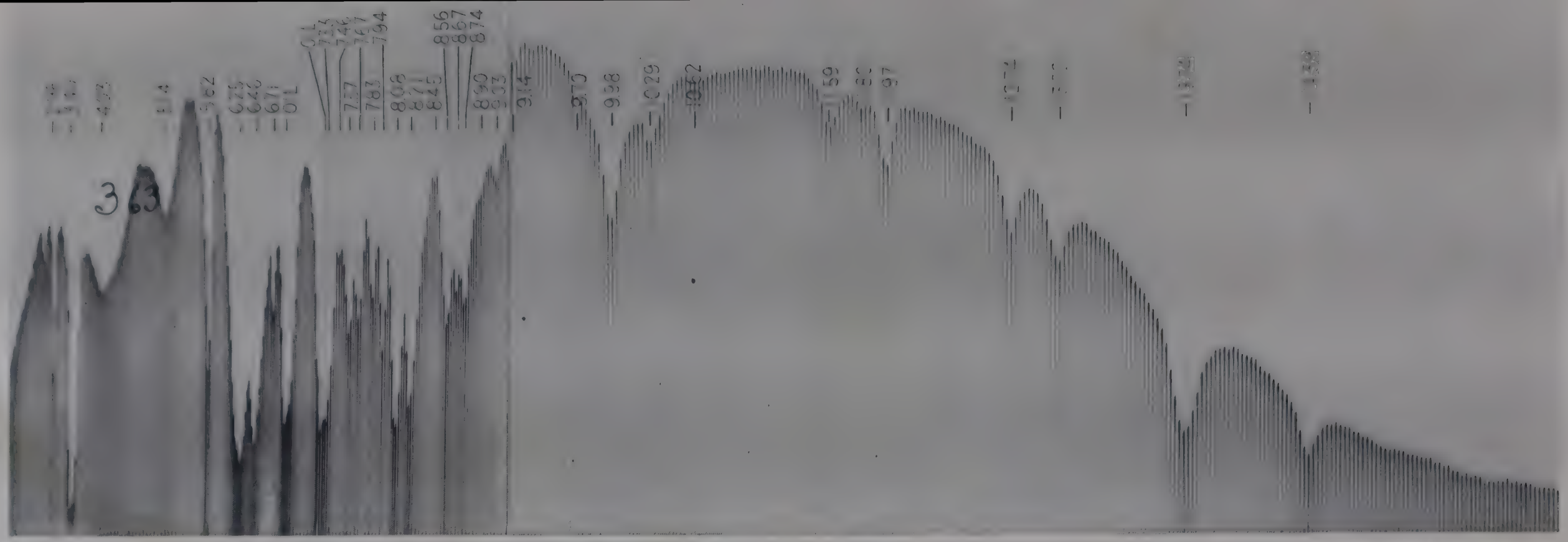


PLATE 97. 5.78 μ Ester C=O; 6.10 μ Amide I; 6.43 μ Amide II; 6.23 μ, 6.69 μ Phenyl. Oil paste

α-PHENACETAMIDO-n-VALERIC ACID

PLATE 96. Assignments: 5.82 μ Acid C=O; 6.25 μ Amide I; 6.46 μ Amide II Preparation: Oil paste

α-PHENACETAMIDO-n-VALERIC ACID

$C_2H_5-CH_2-CH-CO_2H$

$NH-CO-CH_2-C_6H_5$

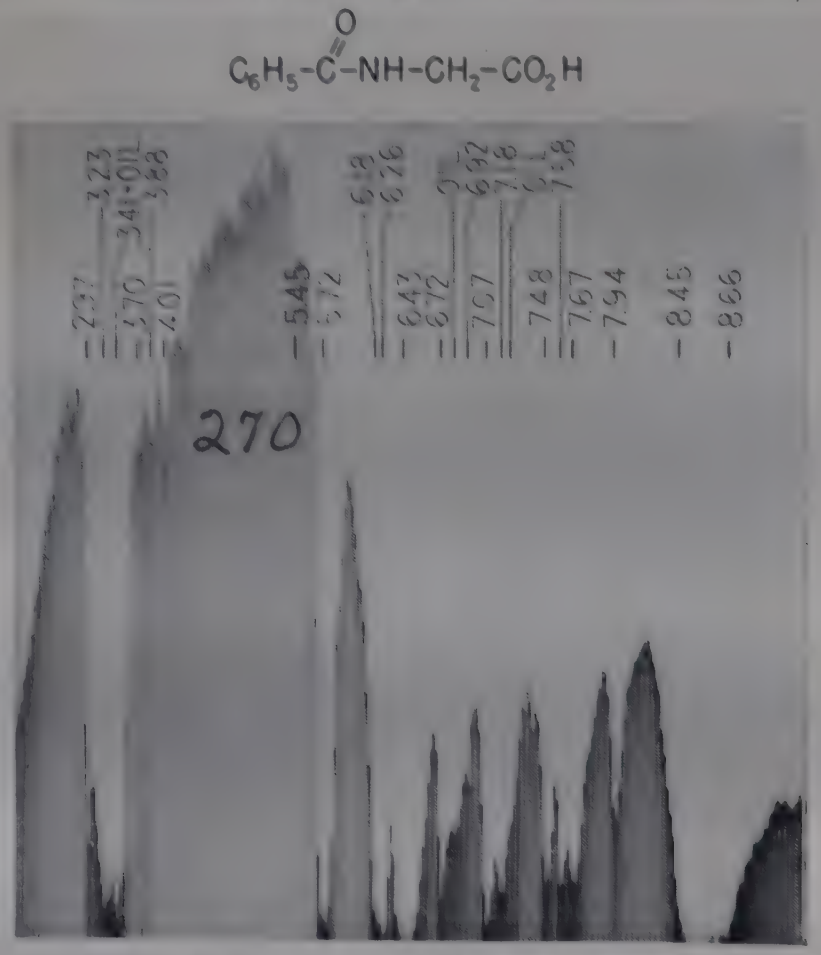


PLATE 98. Assignments: 5.72 μ Acid C=O
6.26 μ Amide I
6.43 μ Amide II
Preparation: Oil paste

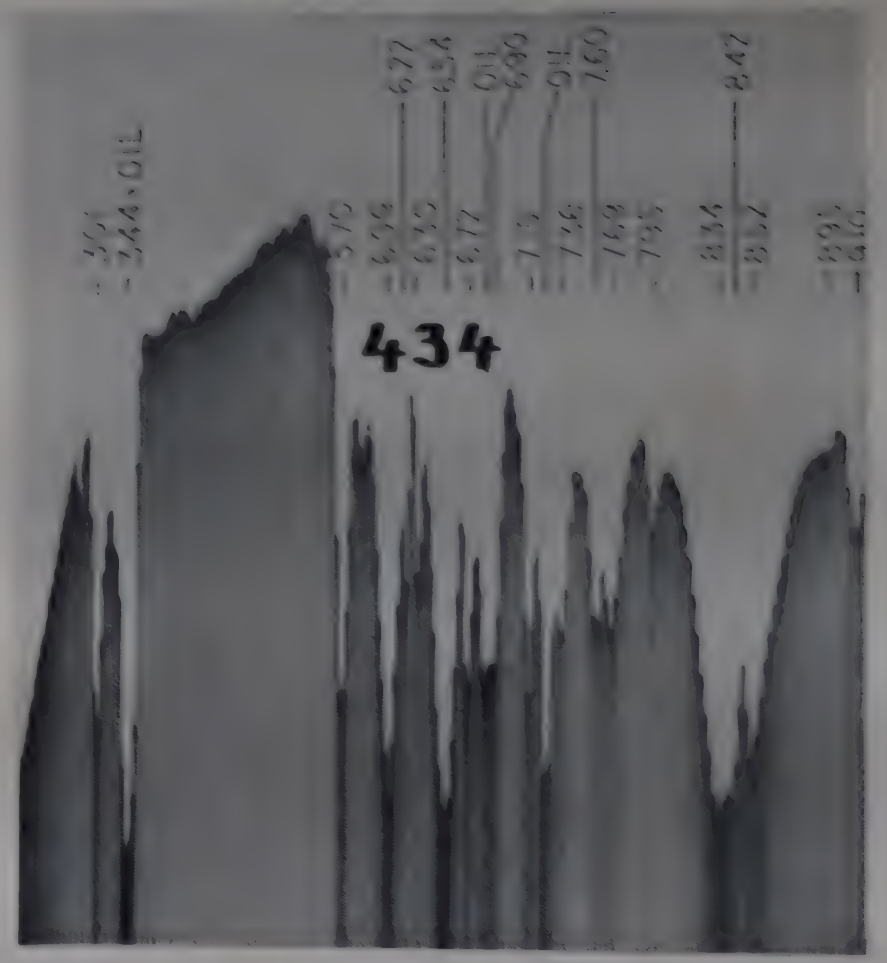


PLATE 99. Assignments: 5.70 μ Ester C=O
6.09 μ Amide I
6.54 μ Amide II
6.22 μ, 6.30 μ, 6.72 μ Phenyl
Preparation: Oil paste

PHENACETURIC ACID

$C_6H_5-CH_2-CO-NH-CH_2-CO_2H$

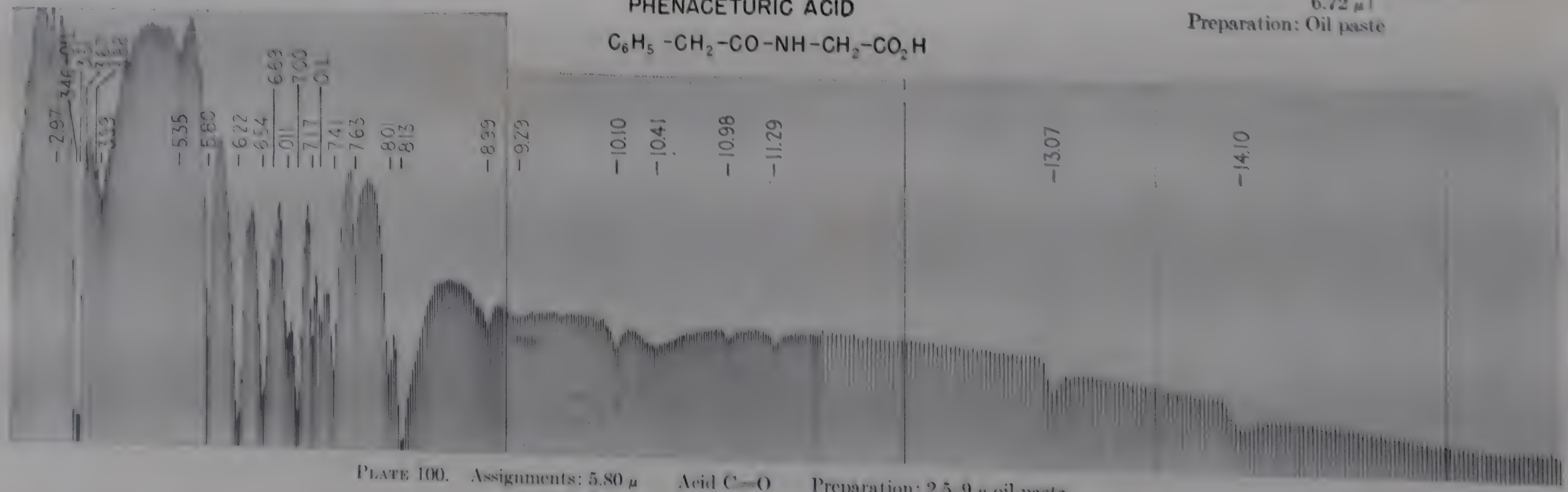


PLATE 100. Assignments: 5.80 μ Acid C=O
6.22 μ Amide I
6.54 μ Amide II
Preparation: 2.5–9 μ oil paste
9–15 μ deposited from ethanol

PHENACETURIC ACID METHYL ESTER

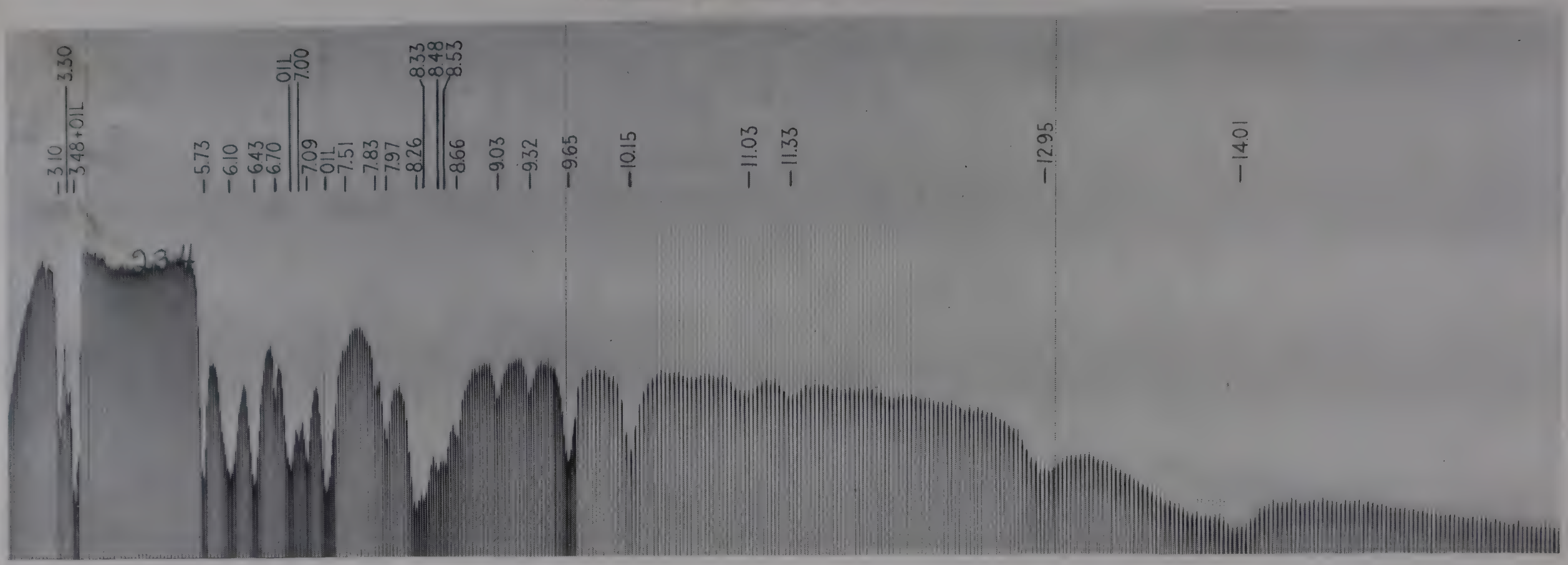


PLATE 101. 5.73 μ Ester C=O; 6.10 μ Amide I; 6.43 μ Amide II. Oil paste

ε-BENZAMIDOCAPROIC ACID

$$C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_5-CO_2H$$

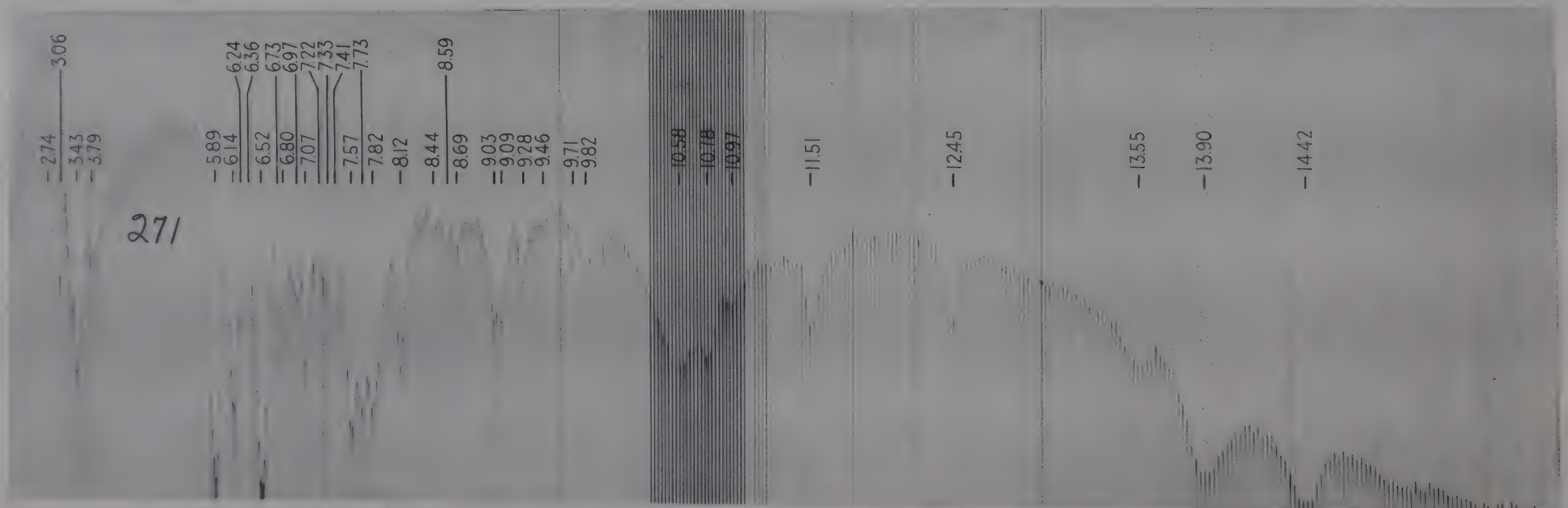


PLATE 103. 5.89 μ Acid C=O; 6.14 μ Amide I; 6.52 μ Amide II; 6.24 μ, 6.36 μ, 6.73 μ Conj. phenyl. Dep. from cyclohexanone

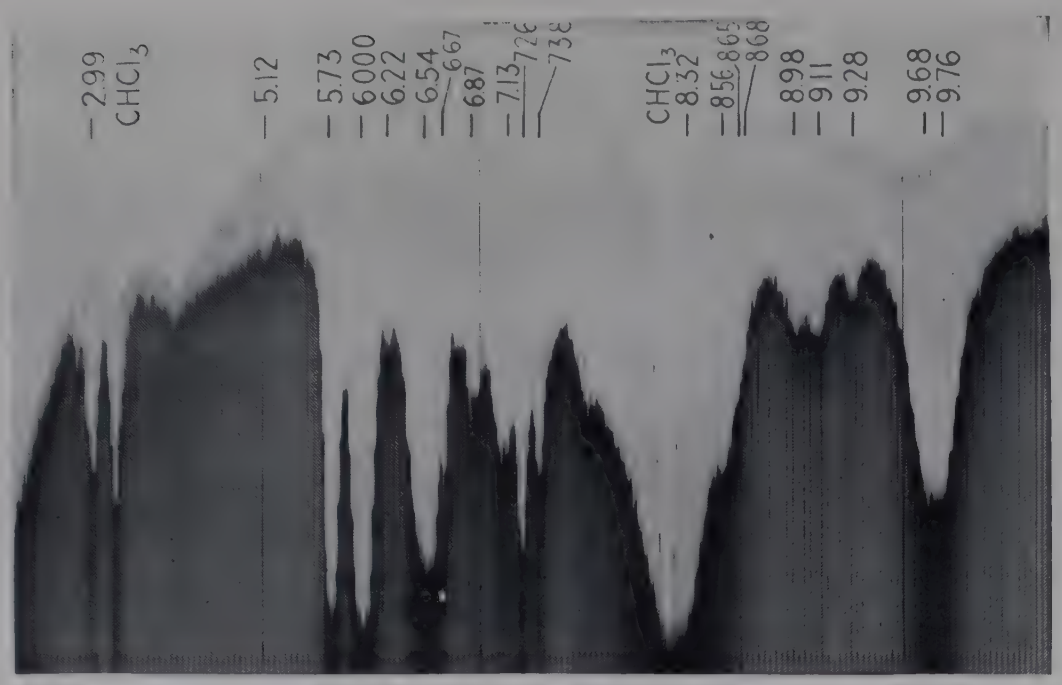


PLATE 102a. Assignments: 5.73 μ Ester C=O
6.00 μ Amide I
6.54 μ Amide II
6.22 μ, 6.67 μ Phenyl
Preparations: Saturated solution in $CHCl_3$, 0.02 mm.

PHENACETURIC ACID ETHYL ESTER
(Top Left and Bottom)

ϵ-BENZAMIDOCAPROIC ACID METHYL ESTER

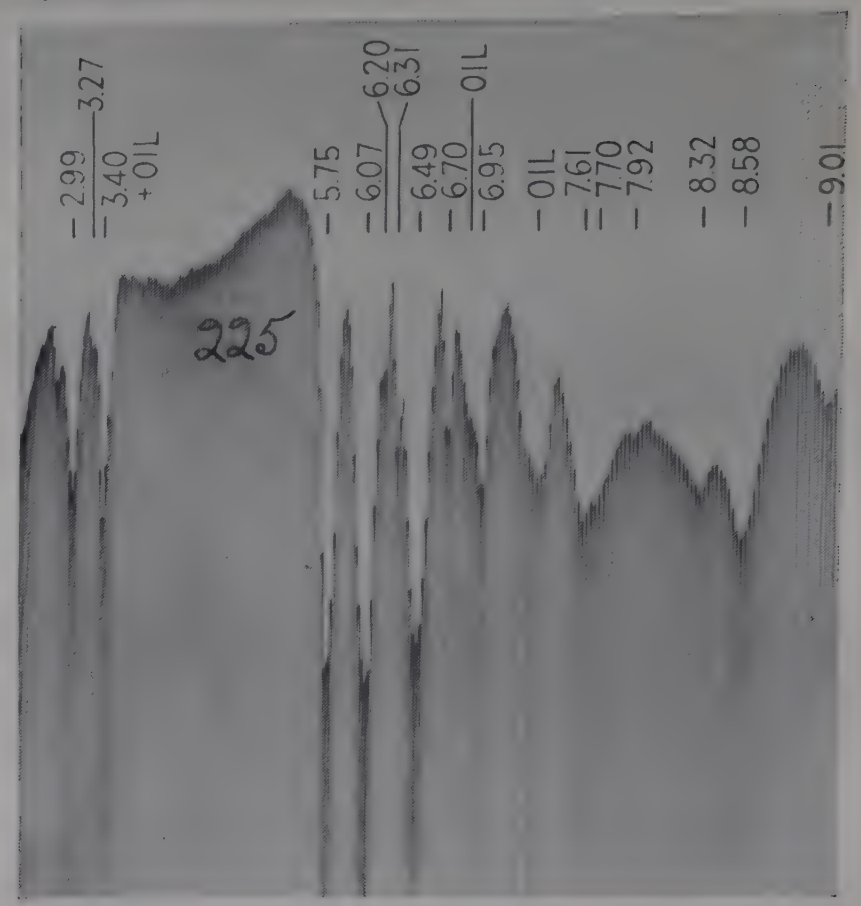


PLATE 104. 5.75 μ Ester C=O: 6.07 μ Amide I; 6.49 μ Amide II; 6.20 μ, 6.31 μ, 6.70 μ Conj. phenyl. Cap. cell

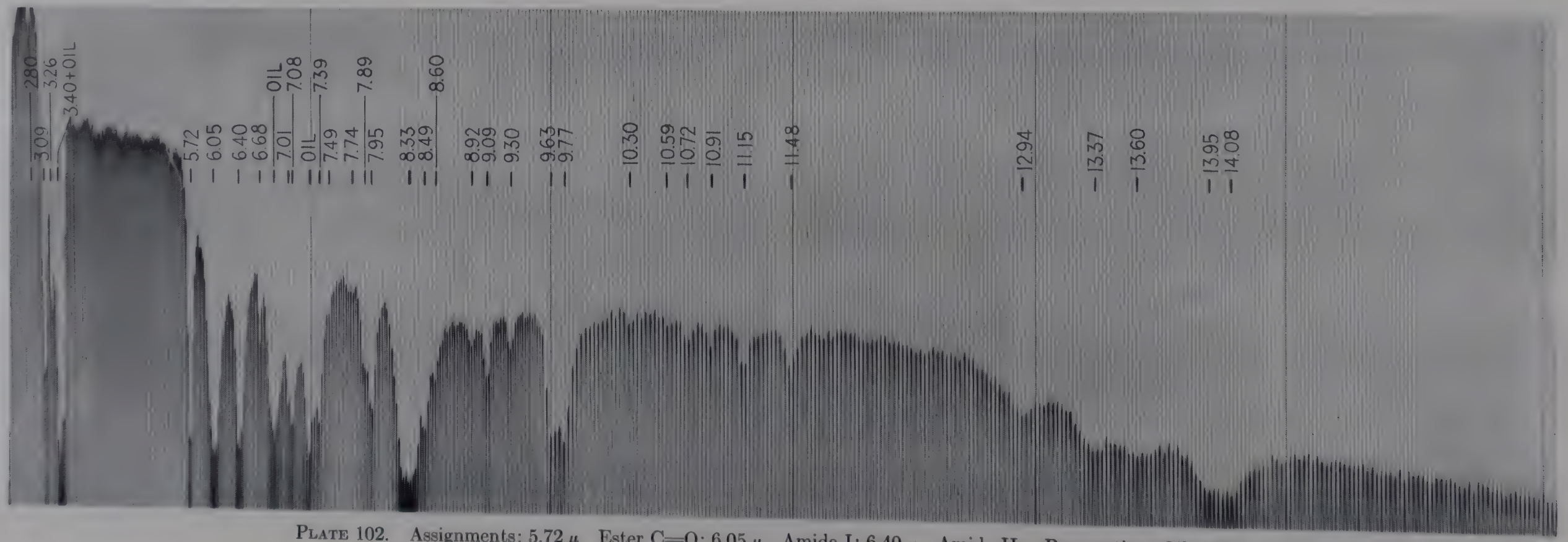


PLATE 102. Assignments: 5.72 μ Ester C=O; 6.05 μ Amide I; 6.40 μ Amide II. Preparation: Oil paste

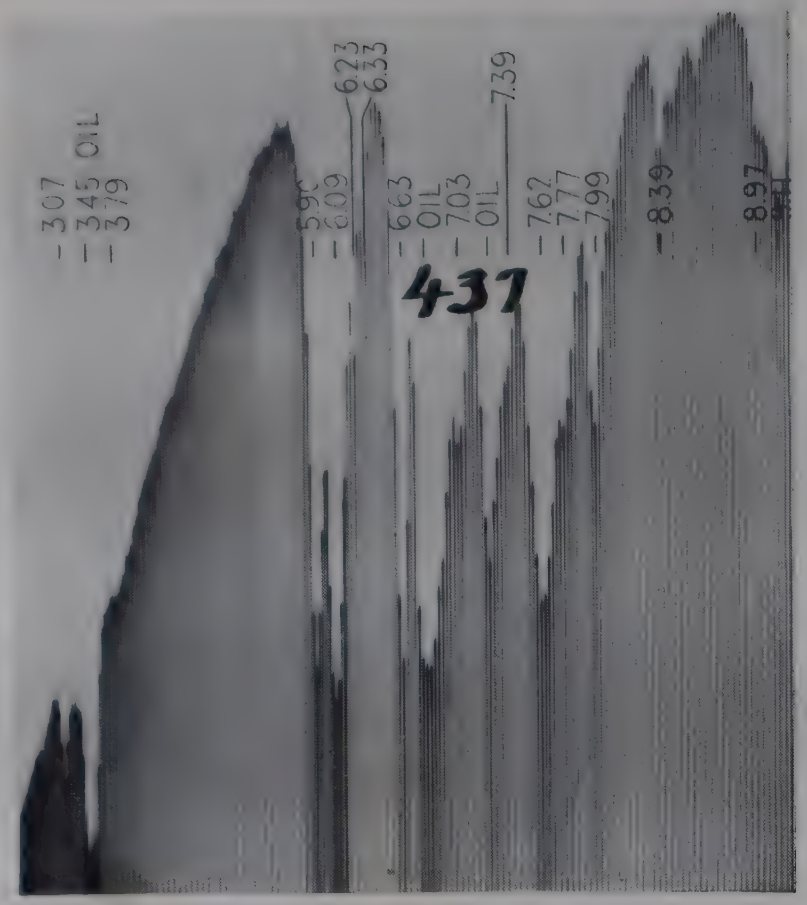
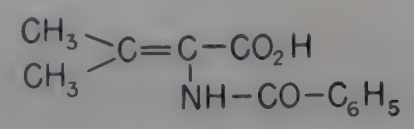


PLATE 105. 5.90 μ Conj. acid C=O; 6.09 μ Amide I, C=C; 6.23 μ, 6.33 μ, 6.63 μ Conj. phenyl; 6.63 μ Amide II. Oil paste

α-BENZAMIDO-β,β-DIMETHYLACRYLIC ACID

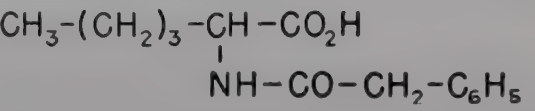


(Top Left)

α-BENZAMIDO-β,β-DIMETHYLACRYLIC ACID METHYL ESTER

(Top Right)

α-PHENACETAMIDO-n-CAPROIC ACID



(Bottom)

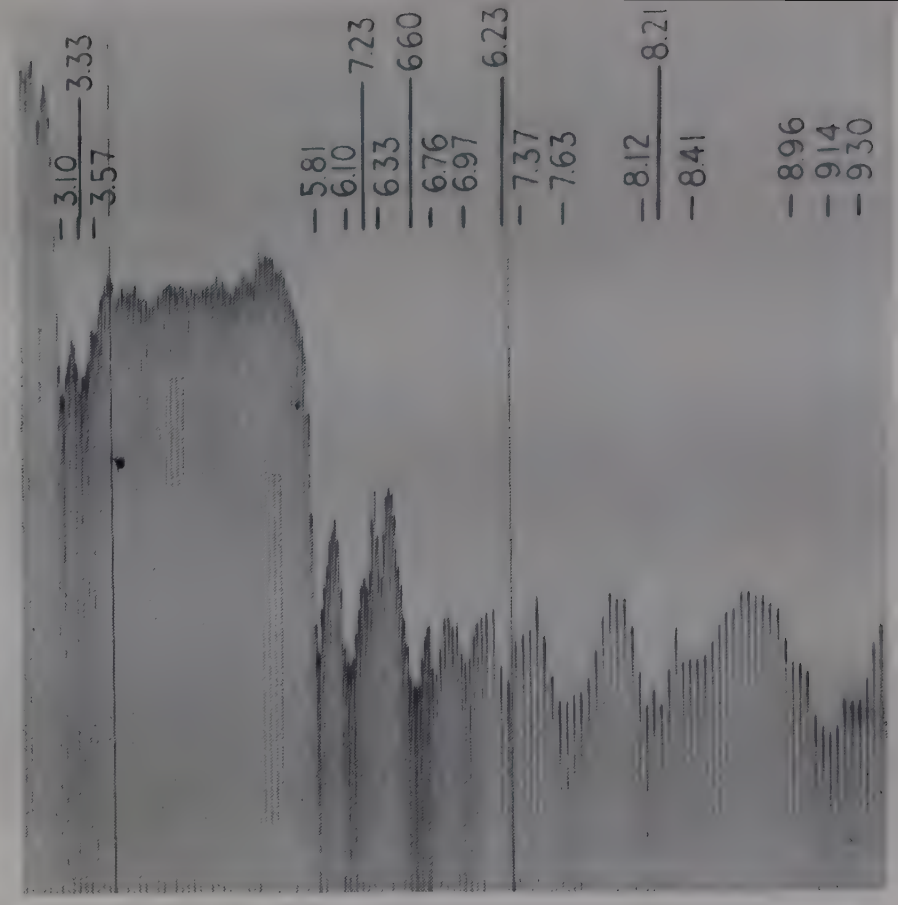


PLATE 106. 5.81 μ Conj. ester C=O; 6.10 μ Amide I; 6.60 μ Amide II; 6.23 μ, 6.31 μ, 6.73 μ Conj. phenyl. Dep. from pyridine

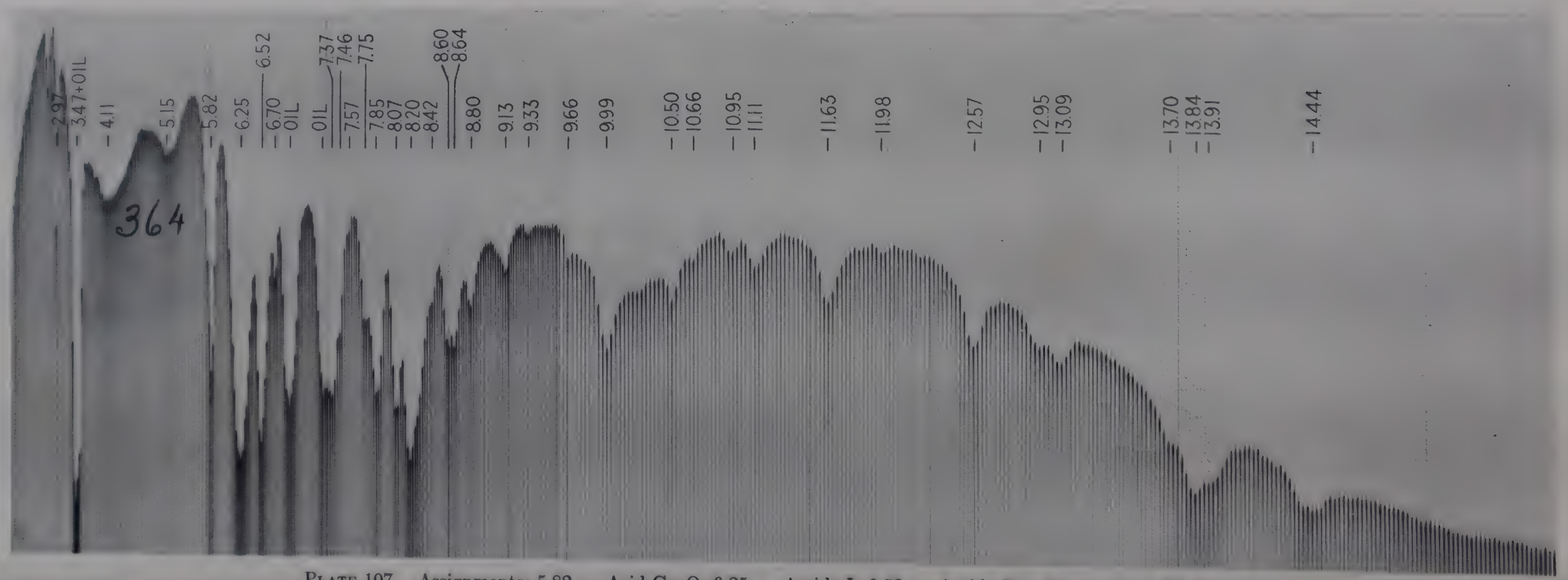


PLATE 107. Assignments: 5.82 μ Acid C=O; 6.25 μ Amide I; 6.52 μ Amide II. Preparation: Oil paste

α-PHENACETAMIDO-n-CAPROIC ACID
METHYL ESTER

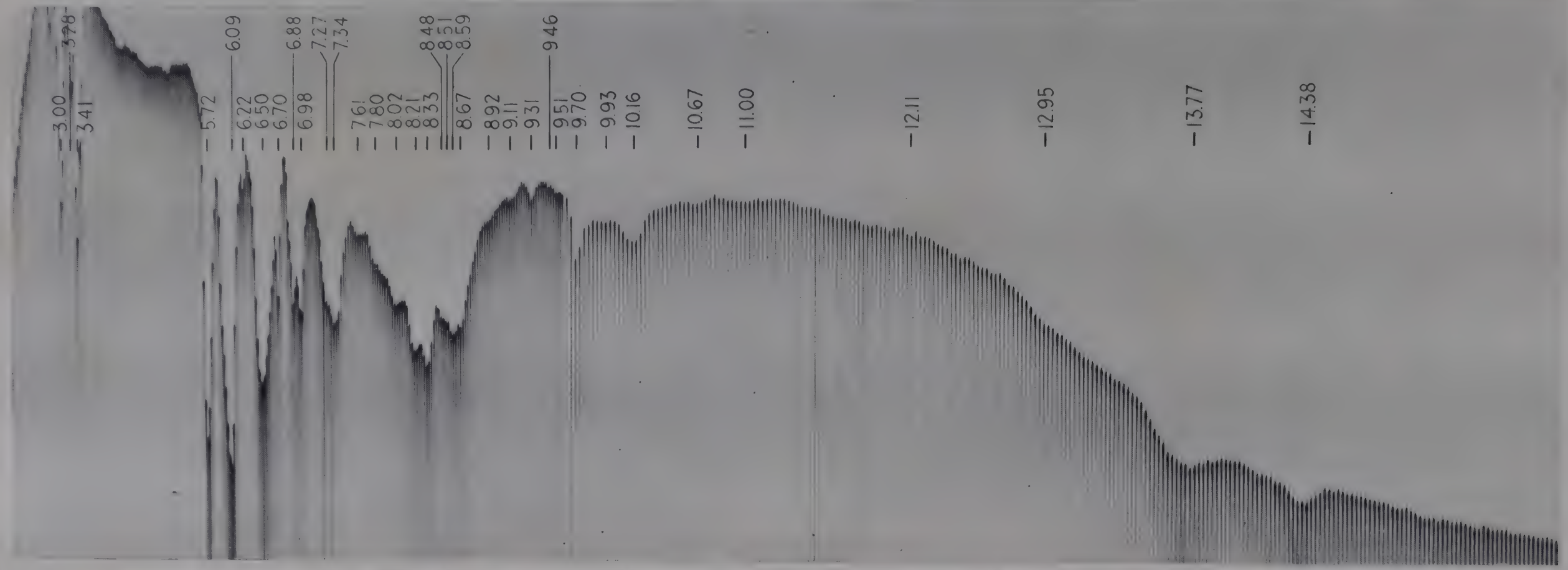
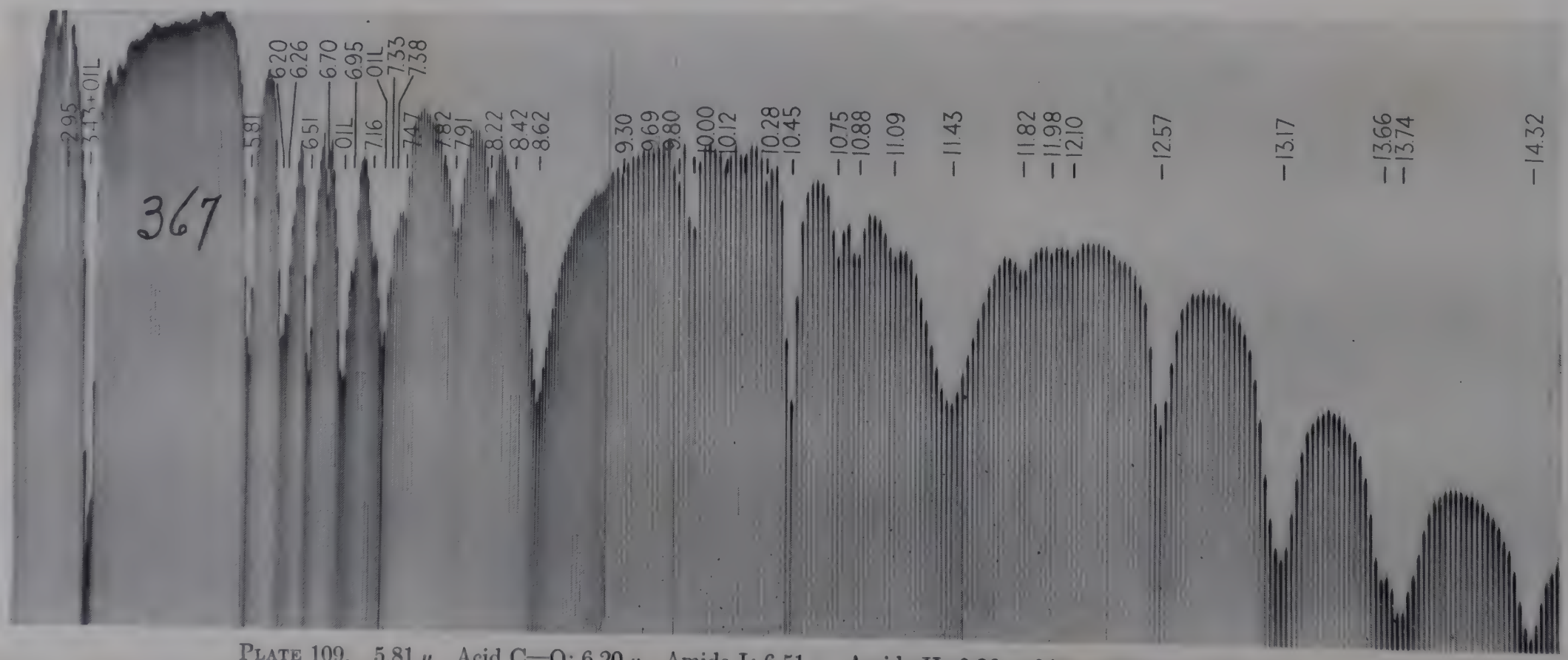


PLATE 108. 5.72 μ Ester C=O; 6.09 μ Amide I; 6.50 μ Amide II; 6.22 μ, 6.70 μ Phenyl. Cap. cell



α-PHENACETAMIDO ISOBUTYRIC ACID

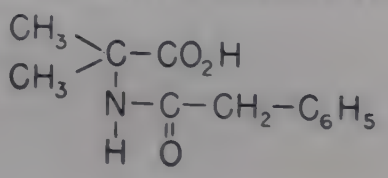


PLATE 109. 5.81 μ Acid C=O; 6.20 μ Amide I; 6.51 μ Amide II; 6.26 μ, 6.70 μ Phenyl. Oil paste

α-PHENACETAMIDO ISOBUTYRIC ACID
METHYL ESTER

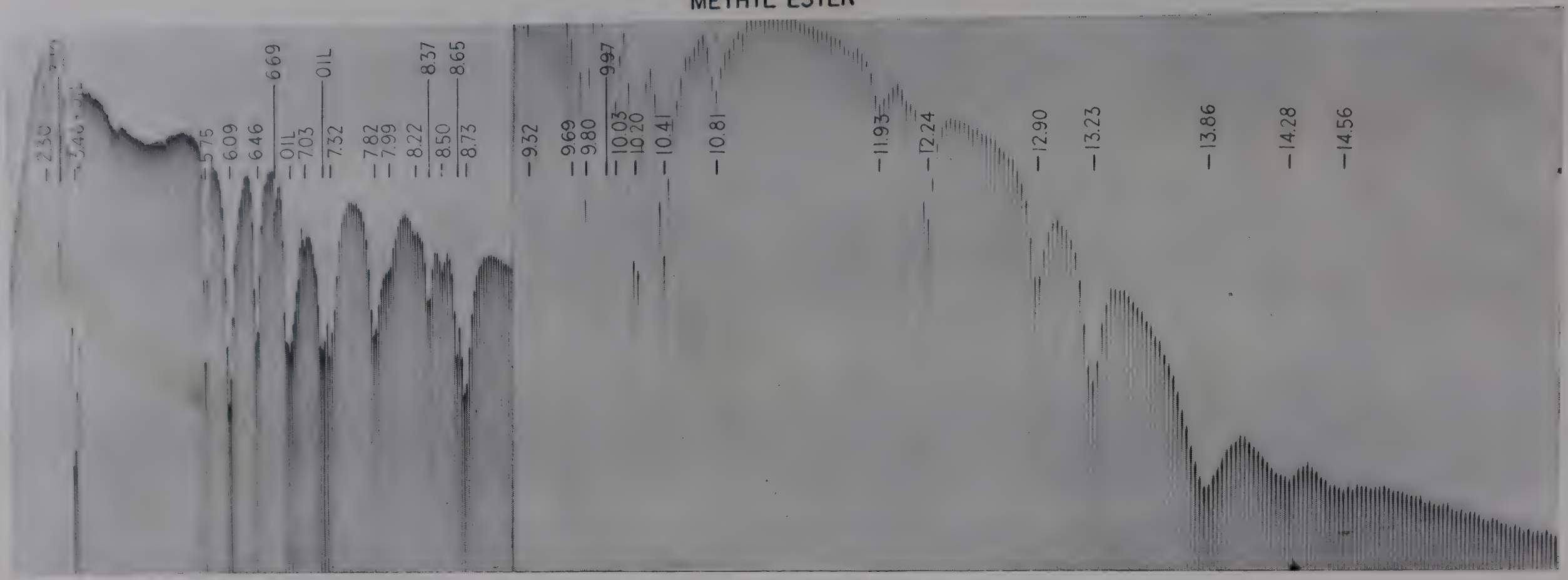
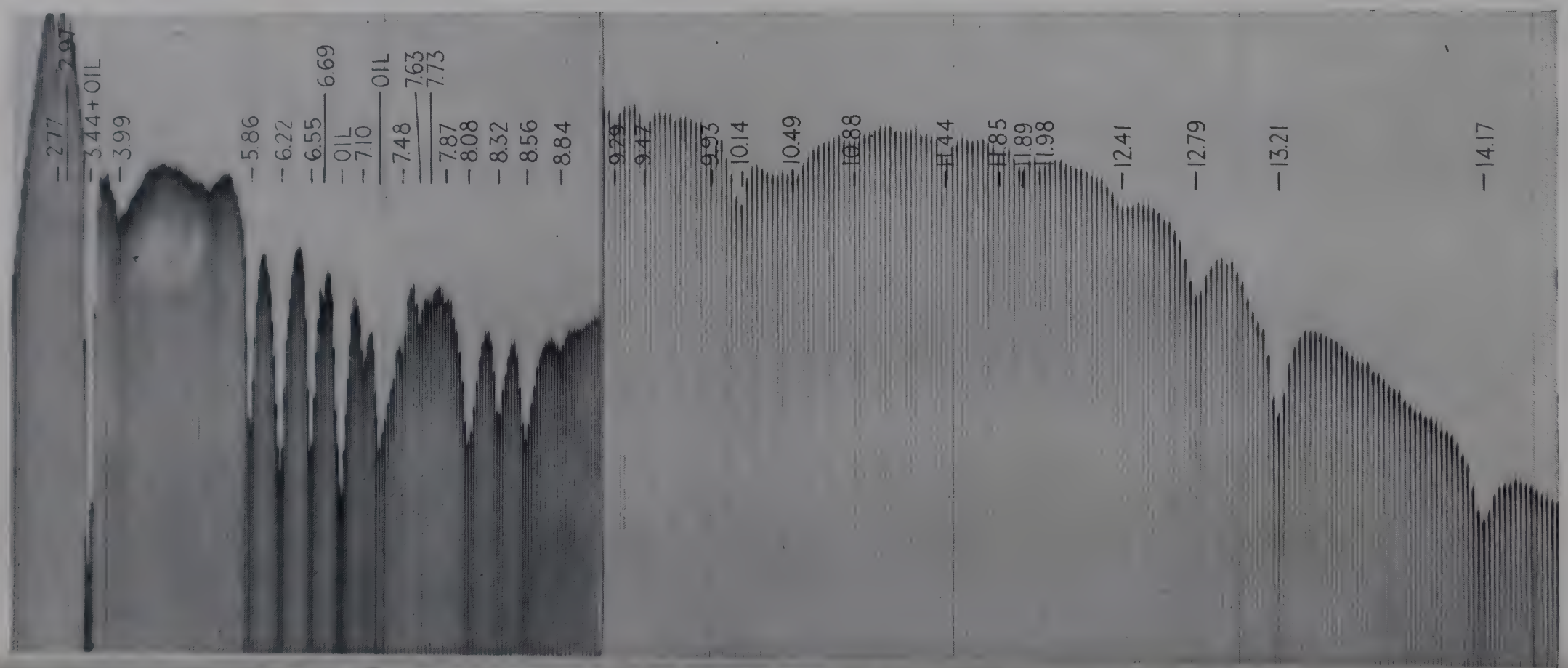
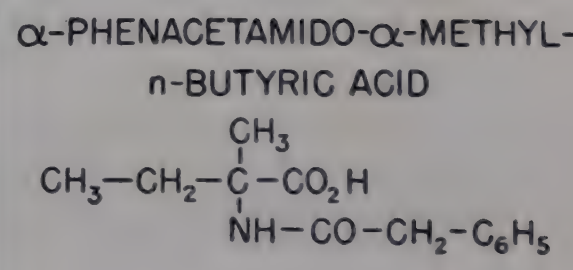


PLATE 110. Assignments: 5.75 μ Ester C=O
6.09 μ Amide I
6.46 μ Amide II
Preparation: Oil paste



α-PHENACETAMIDO-α-METHYL-
n-BUTYRIC ACID



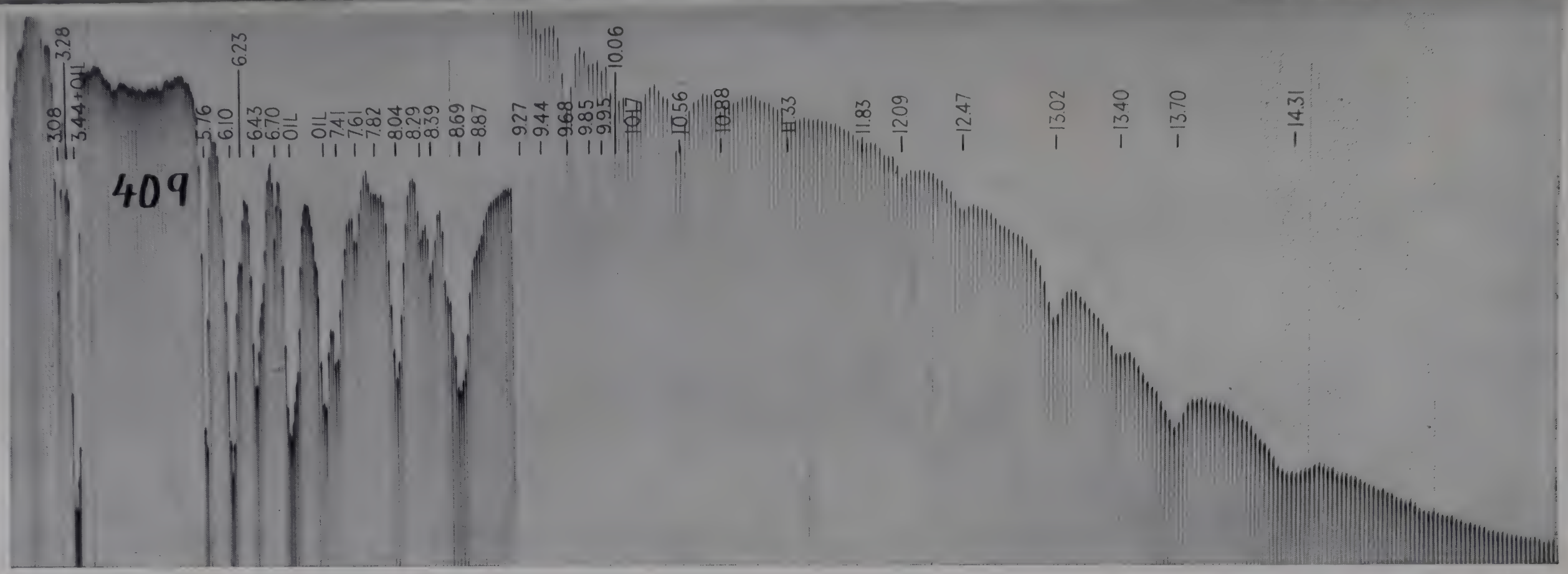


PLATE 112. 5.76 μ Ester C=O; 6.10 μ Amide I; 6.43 μ Amide II; 6.23 μ, 6.70 μ Phenyl. Oil paste

α-PHENACETAMIDO-α-METHYL n-BUTYRIC ACID METHYL ESTER

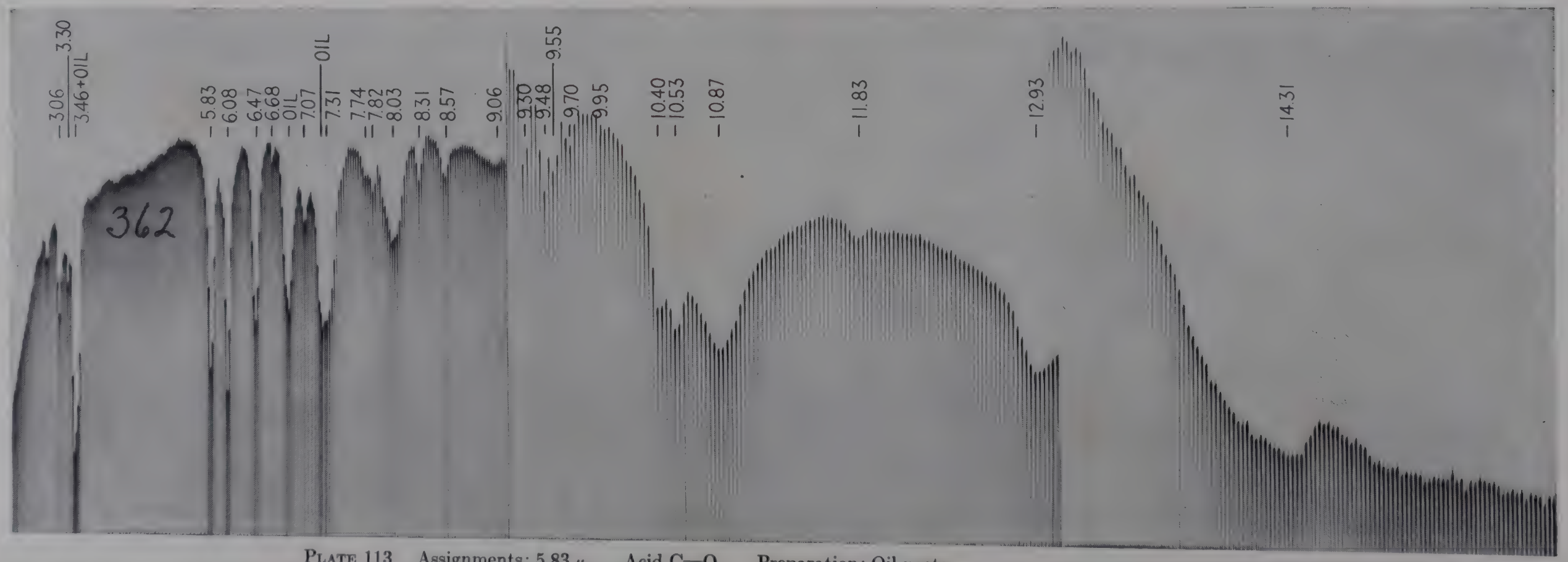


PLATE 113. Assignments: 5.83 μ Acid C=O; 6.08 μ Amide I; 6.47 μ Amide II. Preparation: Oil paste

dl-N-PHENACETYLALANINE

$CH_3-\underset{\underset{NH-CO-CH_2-C_6H_5}{|}}{CH}-CO_2H$

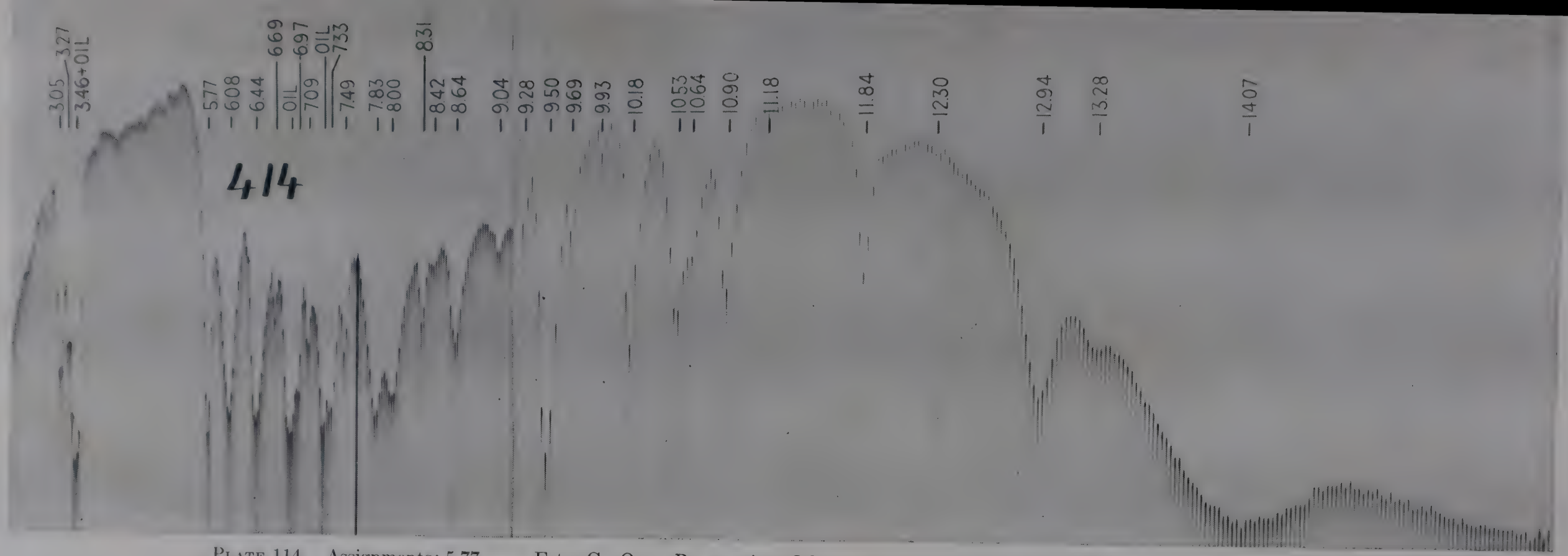


PLATE 114. Assignments: 5.77 μ Ester C=O; 6.08 μ Amide I; 6.44 μ Amide II Preparation: Oil paste

dl-N-PHENACETYLALANINE METHYL ESTER

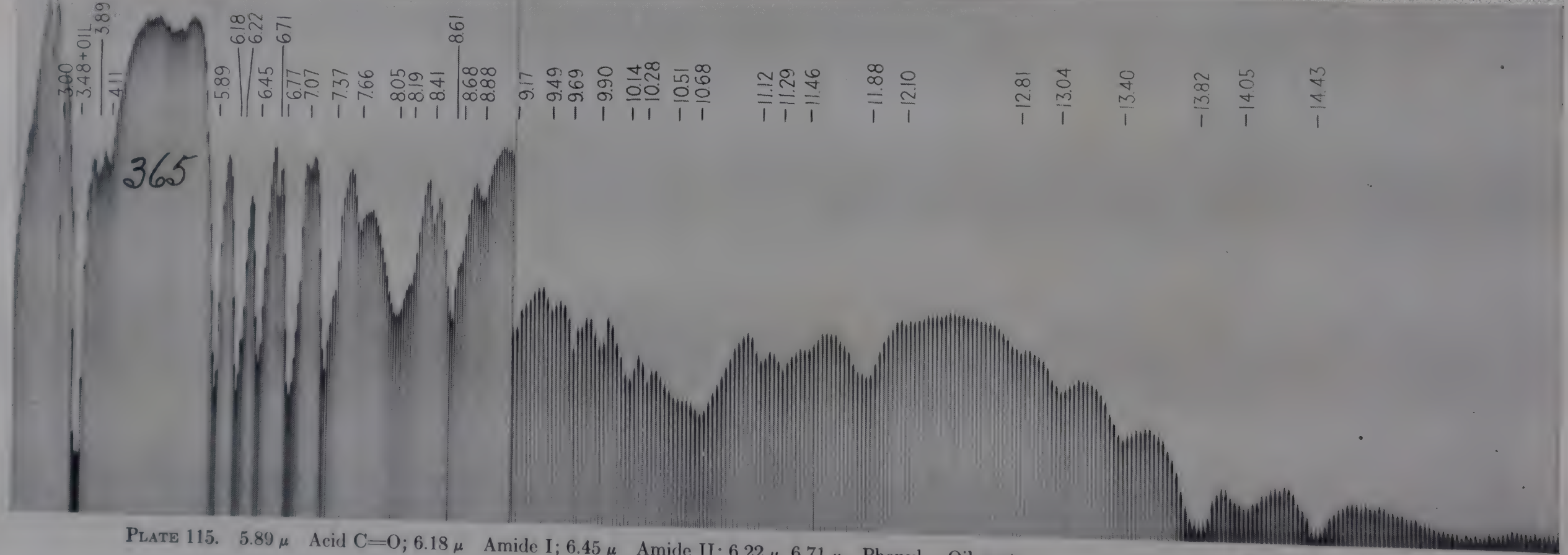


PLATE 115. 5.89 μ Acid C=O; 6.18 μ Amide I; 6.45 μ Amide II; 6.22 μ, 6.71 μ Phenyl. Oil paste

d-N-PHENACETYLISOLEUCINE

$(C_2H_5)(CH_3)-CH-\underset{\underset{NH-CO-CH_2-C_6H_5}{|}}{CH}-CO_2H$

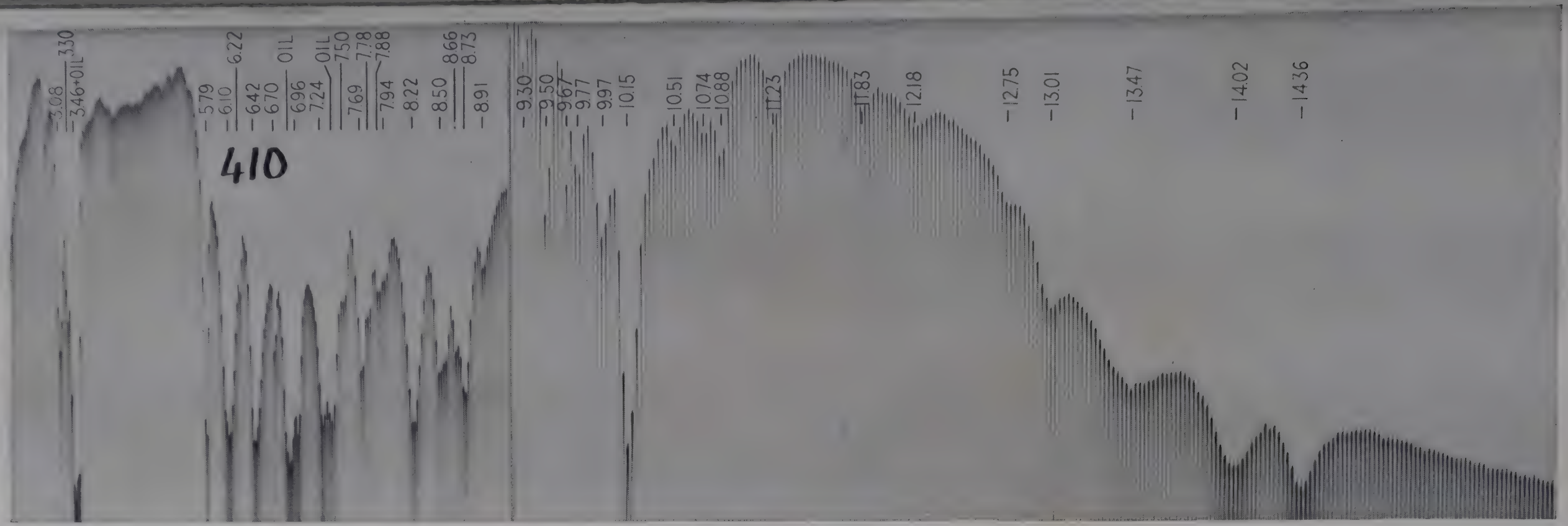


PLATE 116. 5.79 μ Ester C=O; 6.10 μ Amide I; 6.42 μ Amide II; 6.22 μ, 6.70 μ Phenyl. Oil paste

d-N-PHENACETYLISOLEUCINE METHYL ESTER

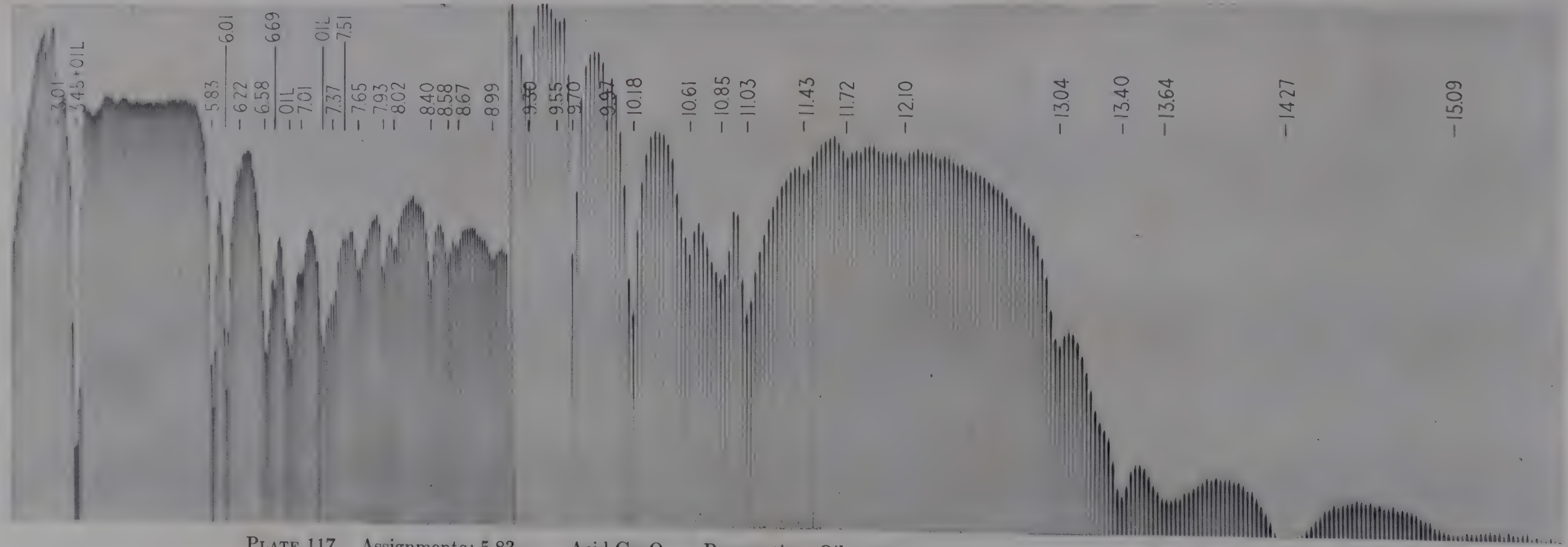


PLATE 117. Assignments: 5.83 μ Acid C=O; 6.01 μ Amide I; 6.58 μ Amide II; 6.22 μ, 6.69 μ Phenyl. Preparation: Oil paste

dl-N-PHENACETYL-β-PHENYLALANINE

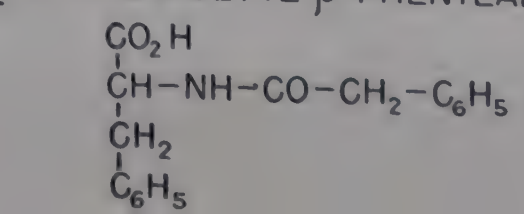


PLATE 118. Assignments: 5.78 μ Ester C=O Preparations: Oil paste

6.03 μ Amide I

6.48 μ Amide II

6.21 μ, 6.69 μ Phenyl

dl-N-PHENACETYL-β-PHENYLALANINE METHYL ESTER

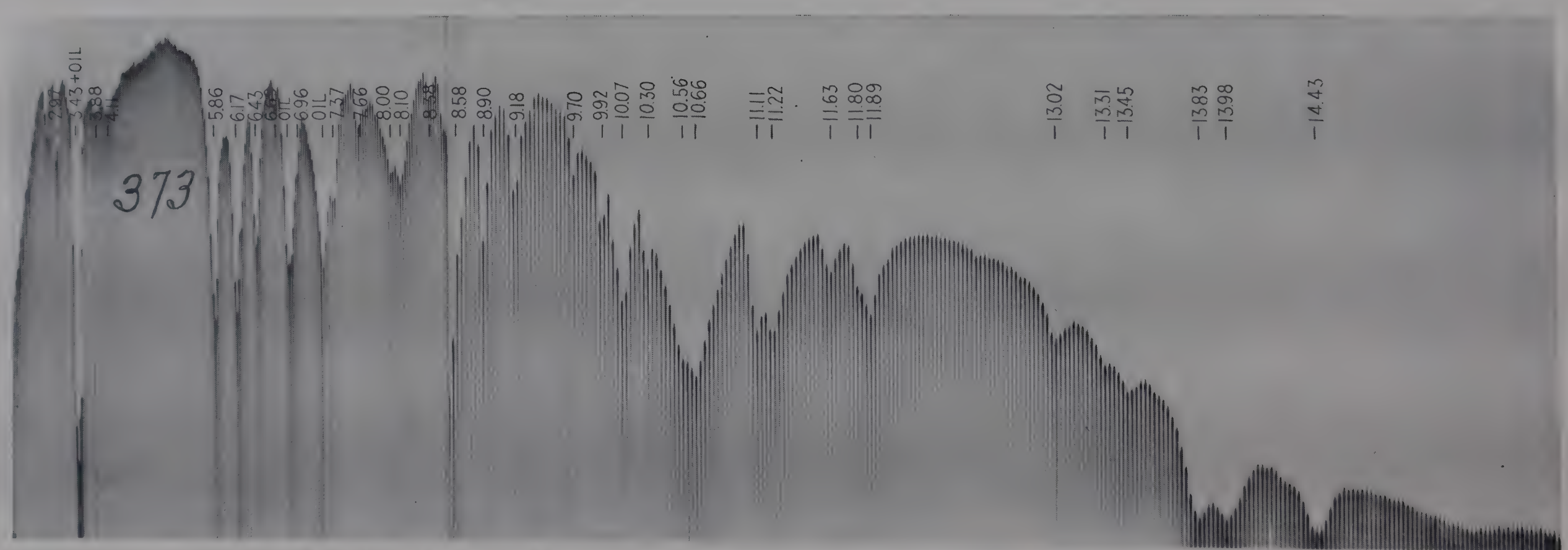


PLATE 119. Assignments: 5.86 μ Acid C=O Preparations: Oil paste

6.17 μ Amide I

6.43 μ Amide II

dl-N-PHENACETYLVALINE

$(CH_3)_2-CH-\underset{|}{CH}-CO_2H$

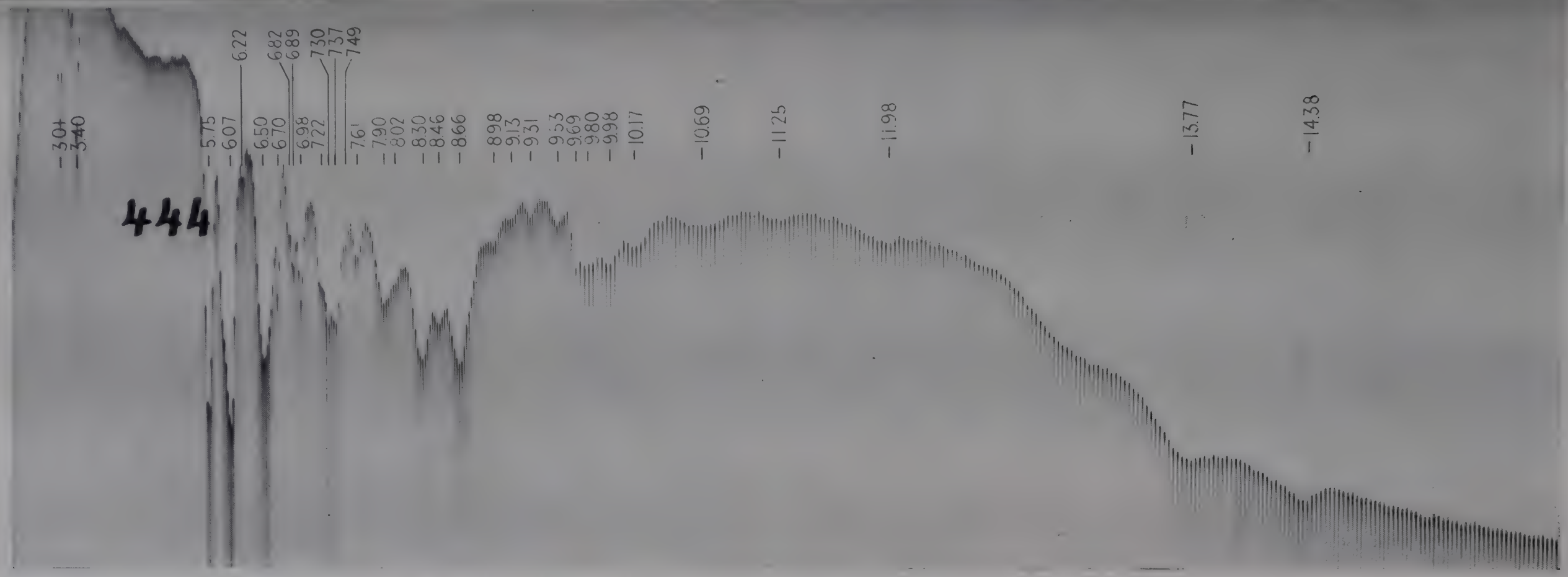


PLATE 120. Assignments: 5.75 μ Ester C=O Preparations: Capillary cell
6.07 μ Amide I
6.50 μ Amide II
6.22 μ } Phenyl
6.70 μ }

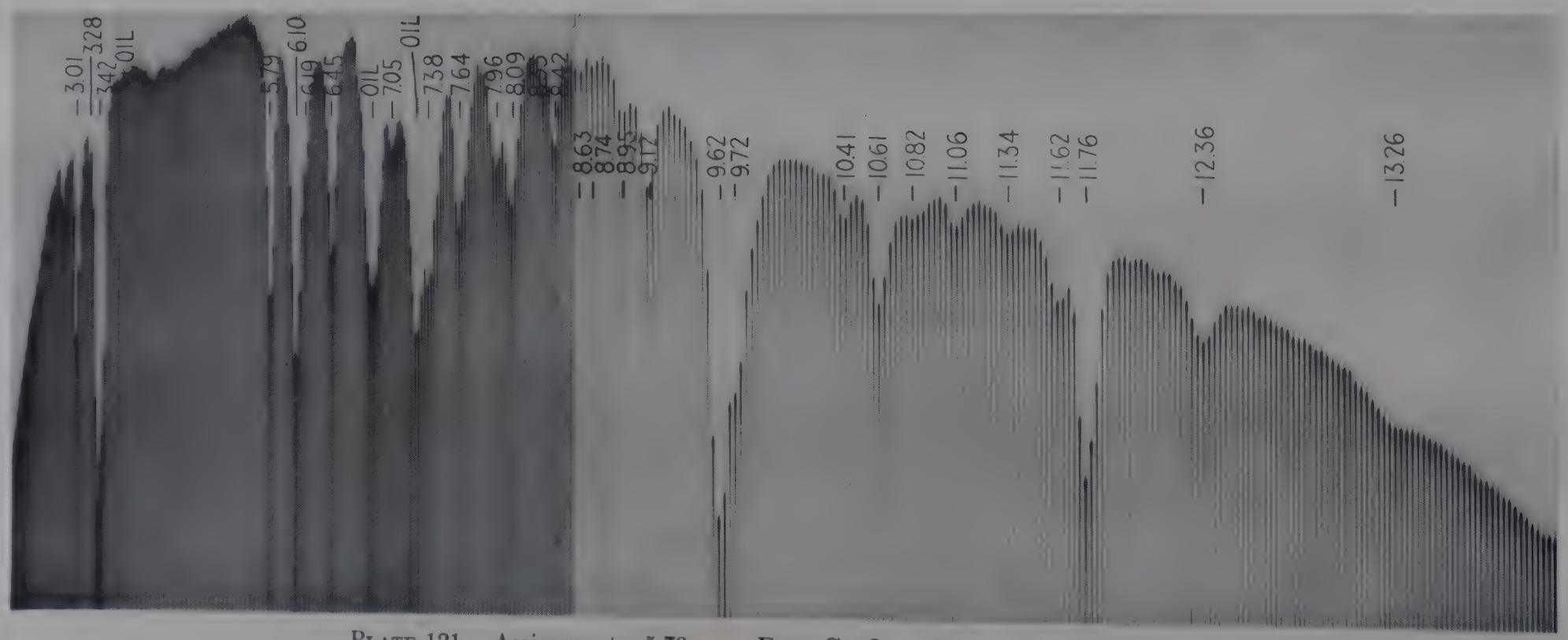
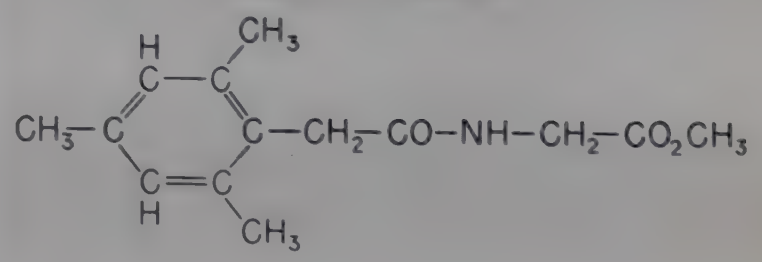
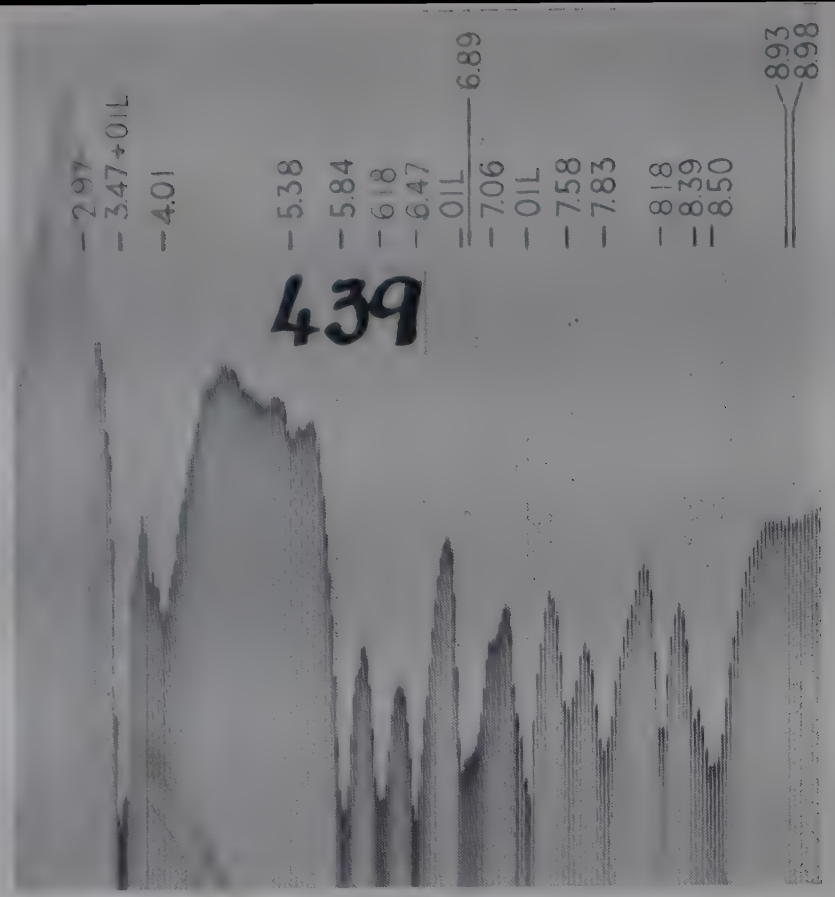


PLATE 121. Assignments: 5.79 μ Ester C=O Preparations: Oil paste
6.10 μ Amide I
6.45 μ Amide II

2,4,6-TRIMETHYLPHENACETURIC ACID METHYL ESTER



α-ACETAMIDOISOBUTYRIC ACID



CH_3, $C-CO_2H$, CH_3 $NH-CO-CH_3$

(Top Left)

PLATE 122. Assignments: 5.84 μ Acid C=O
6.18 μ Amide I
6.48 μ Amide II
Preparations: Oil paste

N-METHYLFORMAMIDE

$H-C(=O)-N(H)-CH_3$

(Top Right)

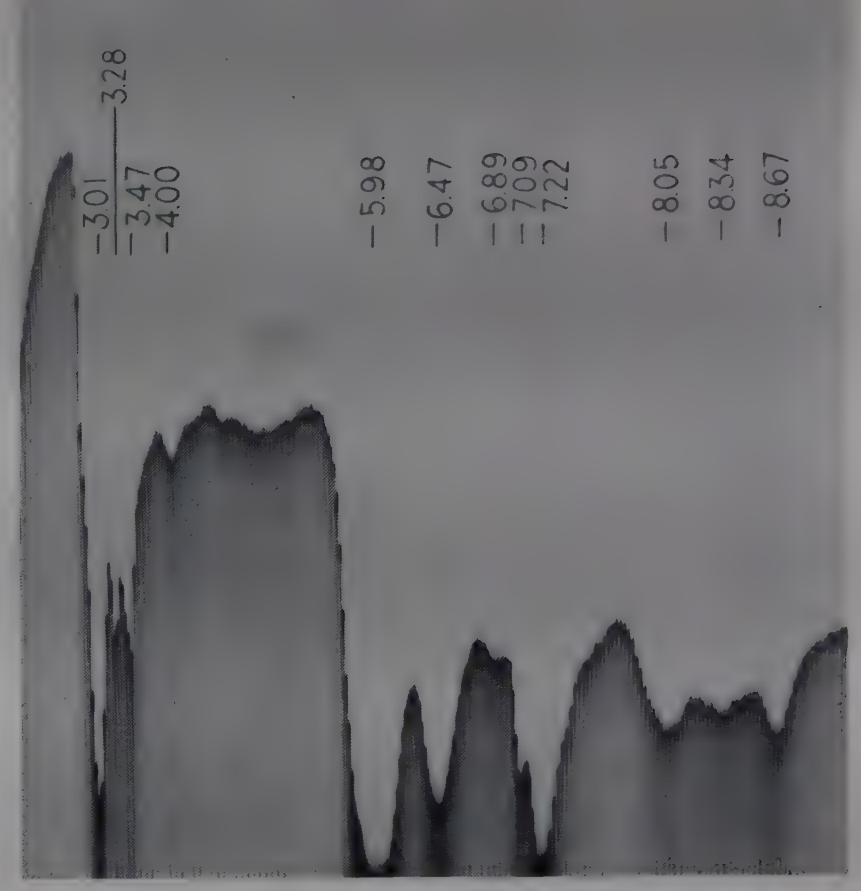


PLATE 123. Assignments: 5.98 μ Amide I
6.47 μ Amide II
Preparations: 0.005 mm.

N-METHYLPHENACETAMIDE

$C_6H_5-CH_2-C(=O)-N(H)-CH_3$

(Bottom Left and Right)

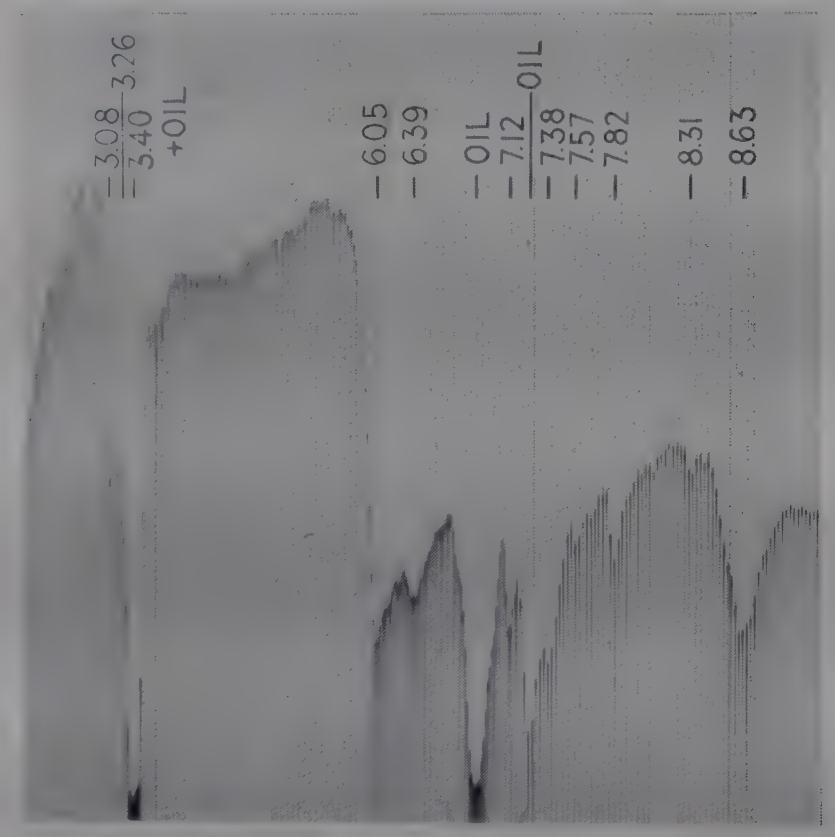


PLATE 125. Assignments: 6.05 μ Amide I
6.39 μ Amide II
Preparations: Oil paste

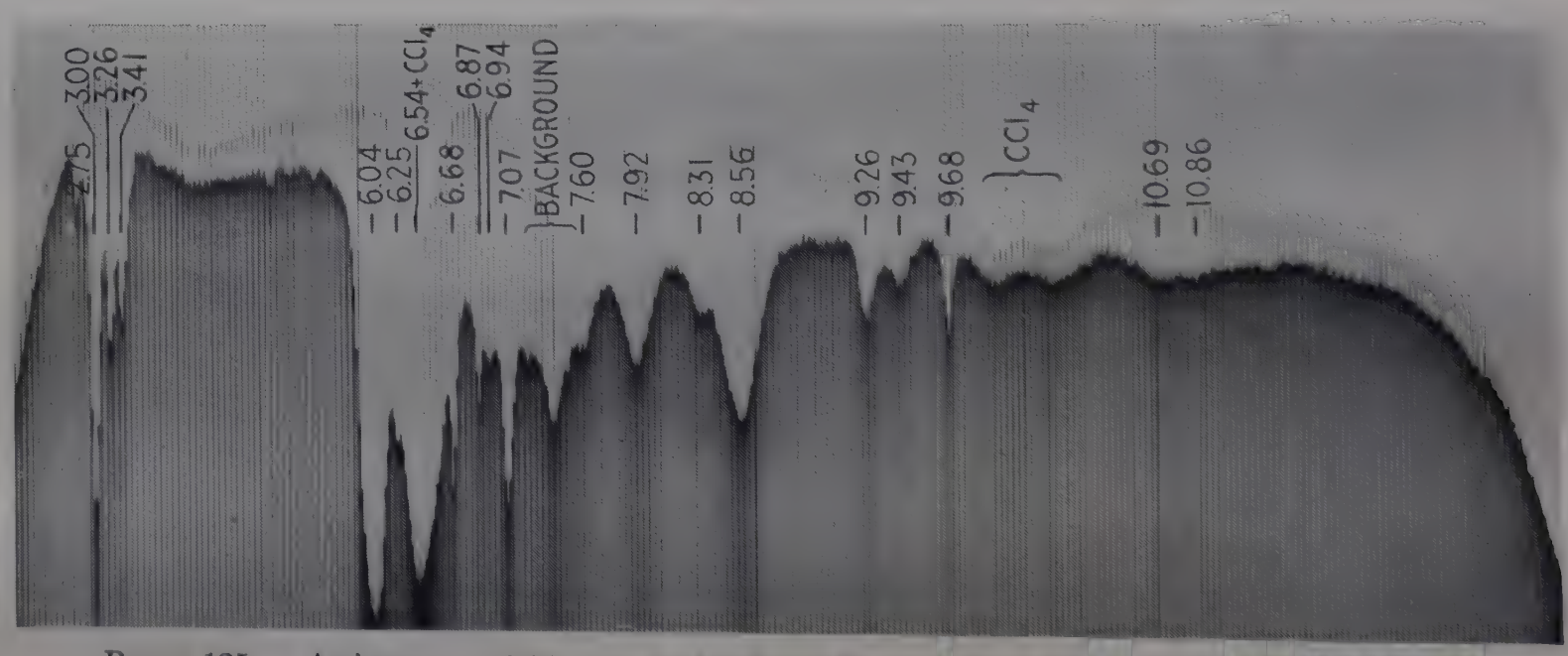


PLATE 125a. Assignments: 6.04 μ Amide I
6.54 μ Amide II
6.25 μ, 6.68 μ Phenyl
Preparations: 5% solution in CCl_4 0.04 mm.

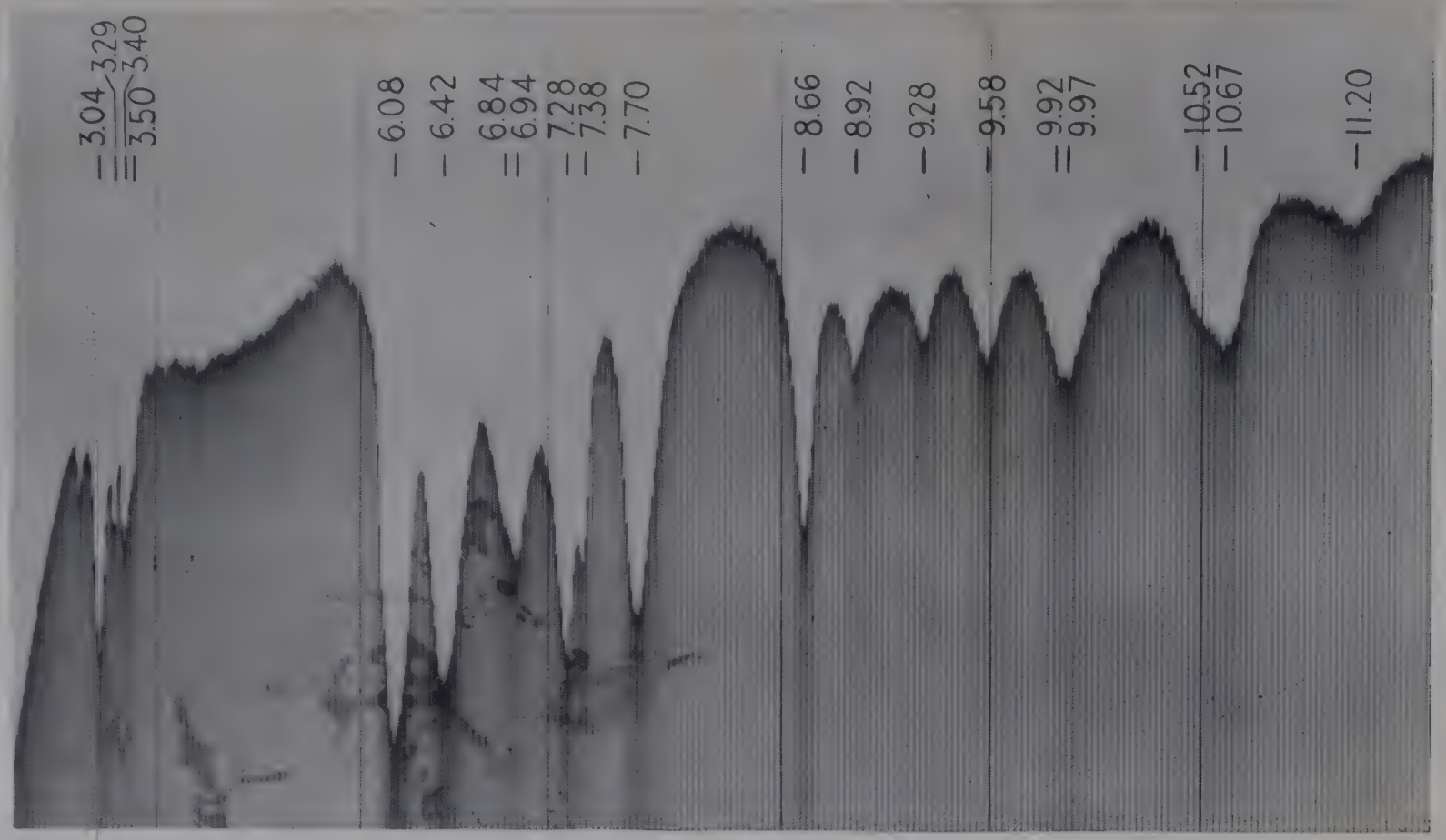
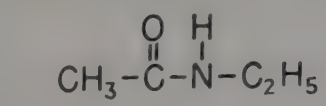


PLATE 126. Assignments: 6.08 μ Amide I Preparations: Capillary cell
6.42 μ Amide II

N-ETHYLACETAMIDE

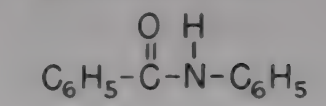


(*Top*)

DEUTERO-N-ETHYLACETAMIDE

(*Bottom Left*)

BENZANILIDE



(*Bottom Right*)

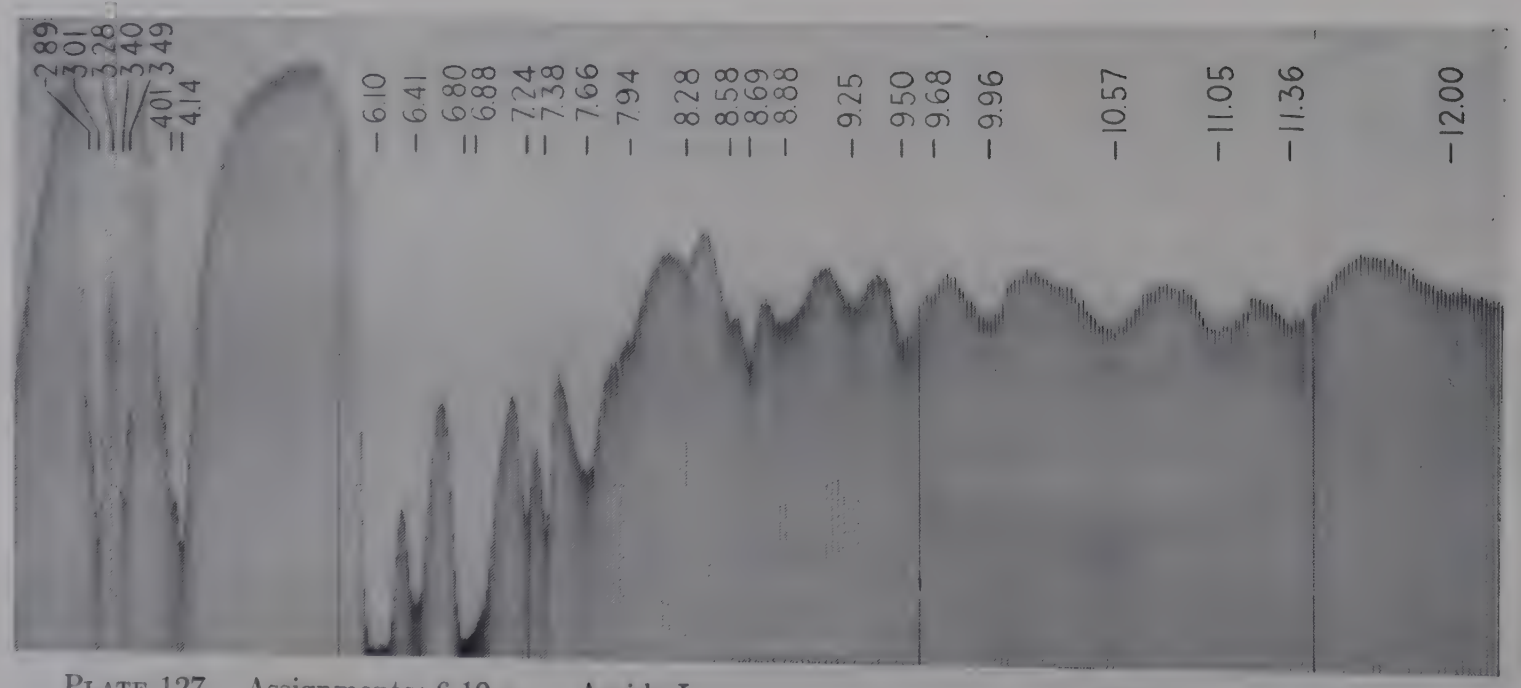


PLATE 127. Assignments: 6.10 μ Amide I
6.41 μ Amide II (undeuterized fraction)
6.80 μ Amide II (deuterized fraction)
Preparations: 0.005 mm.

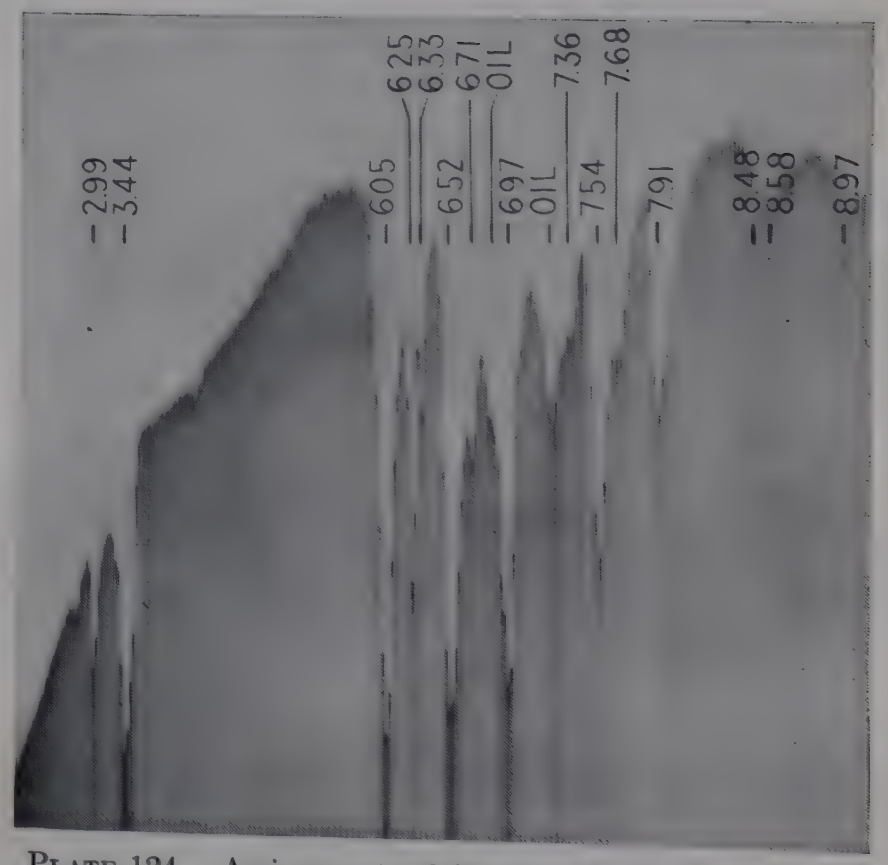


PLATE 124. Assignments: 6.05 μ Amide I
6.52 μ Amide II
6.25 μ, 6.33 μ, 6.71 μ Conjugated phenyl

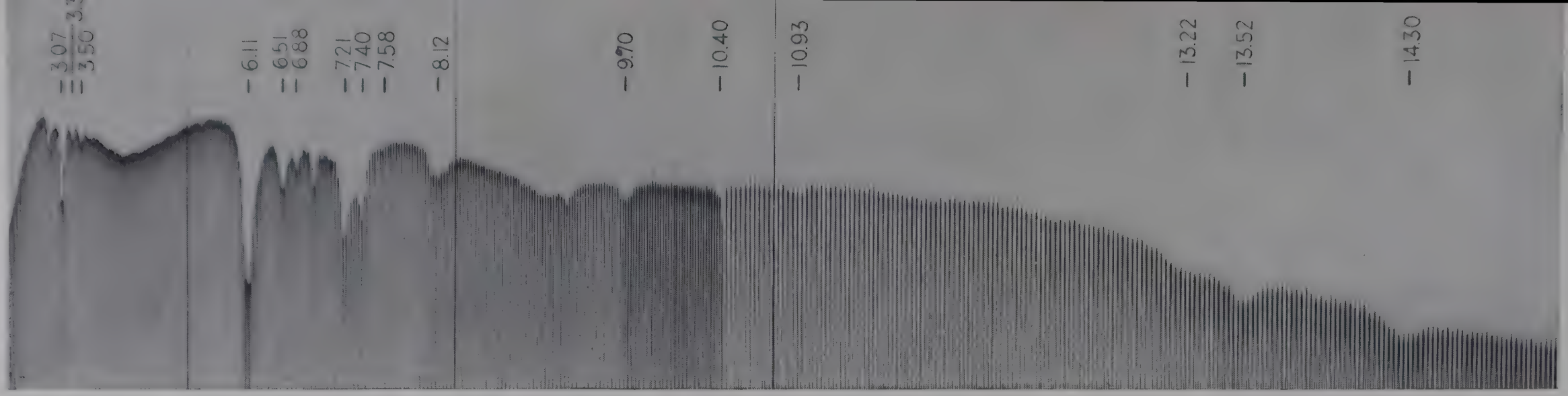


PLATE 128. 6.11 μ Amide I; 6.51 μ Amide II. Dep. from $CHCl_3$

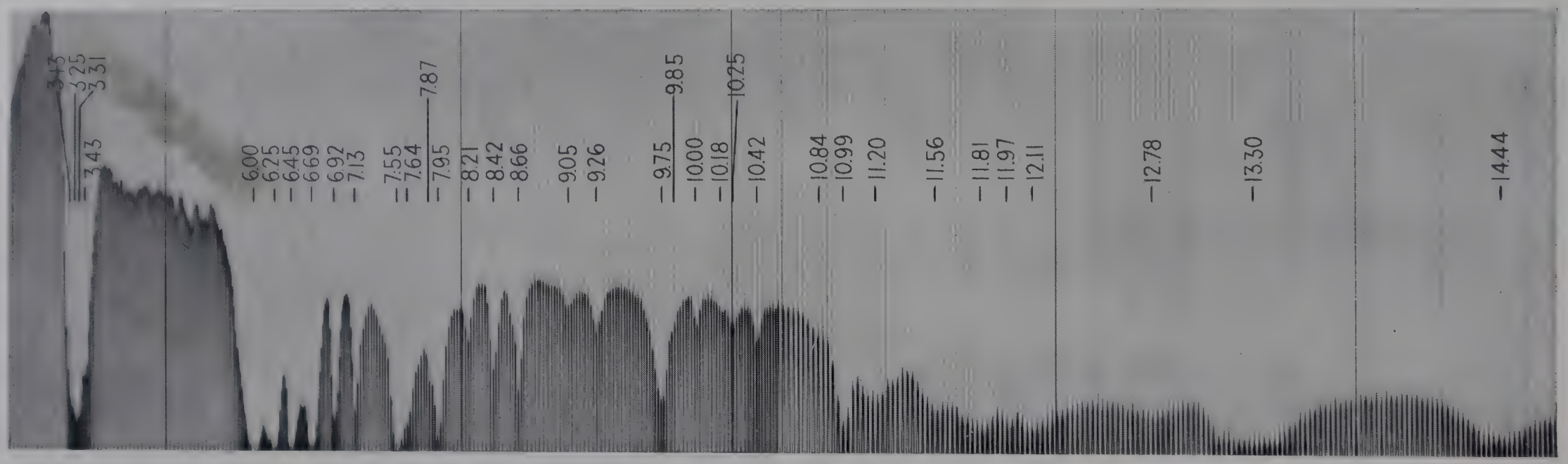


PLATE 129. 6.00 μ Amide I; 6.45 μ Amide II; 6.25 μ, 6.69 μ Phenyl. 0.015 mm.

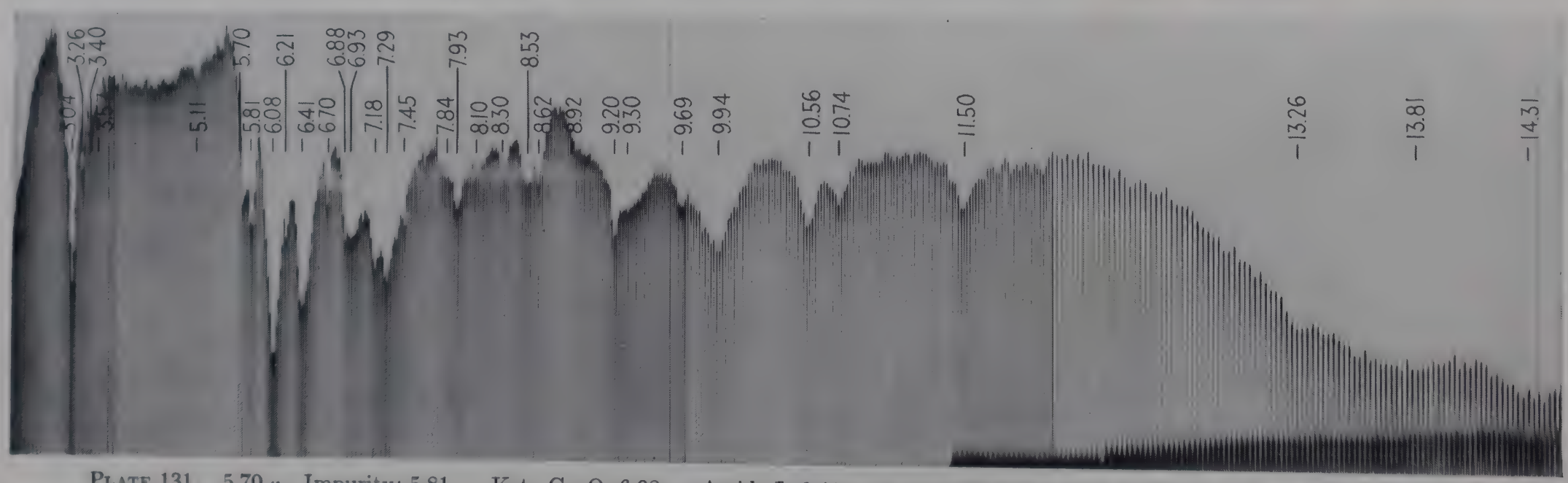
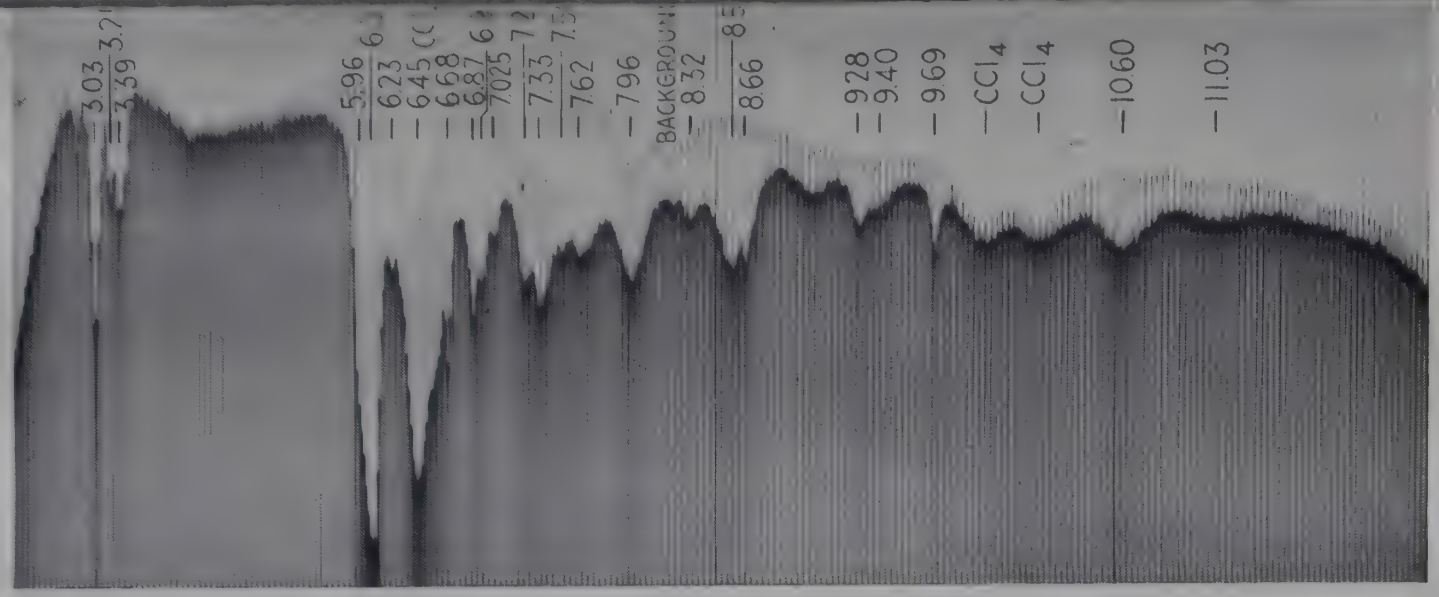


PLATE 131. 5.70 μ Impurity; 5.81 μ Keto C=O; 6.08 μ Amide I; 6.41 μ Amide II; 6.21 μ, 6.70 μ Phenyl. Dep. from acetonitrile



$$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-C_2H_5$$

(Top and Center)

N-METHYLBENZAMIDE

$$C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{N}{N}-CH_3$$

(Bottom)

PLATE 130a. 6.07 μ Amide I; 6.45 μ Amide II; 4% sol, CCl_4. 0.04 mm.

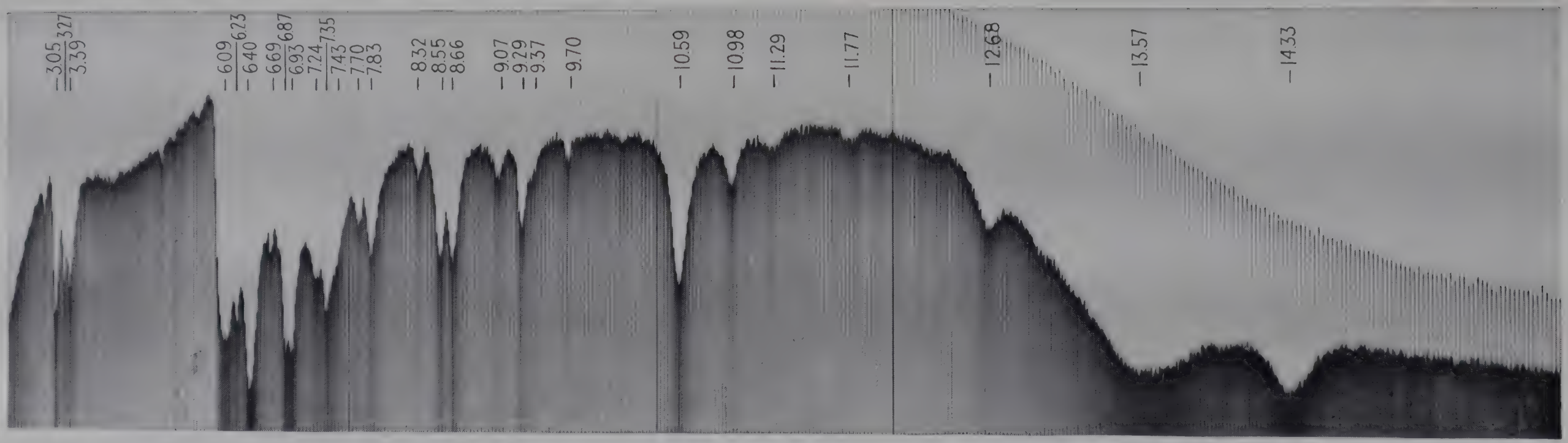
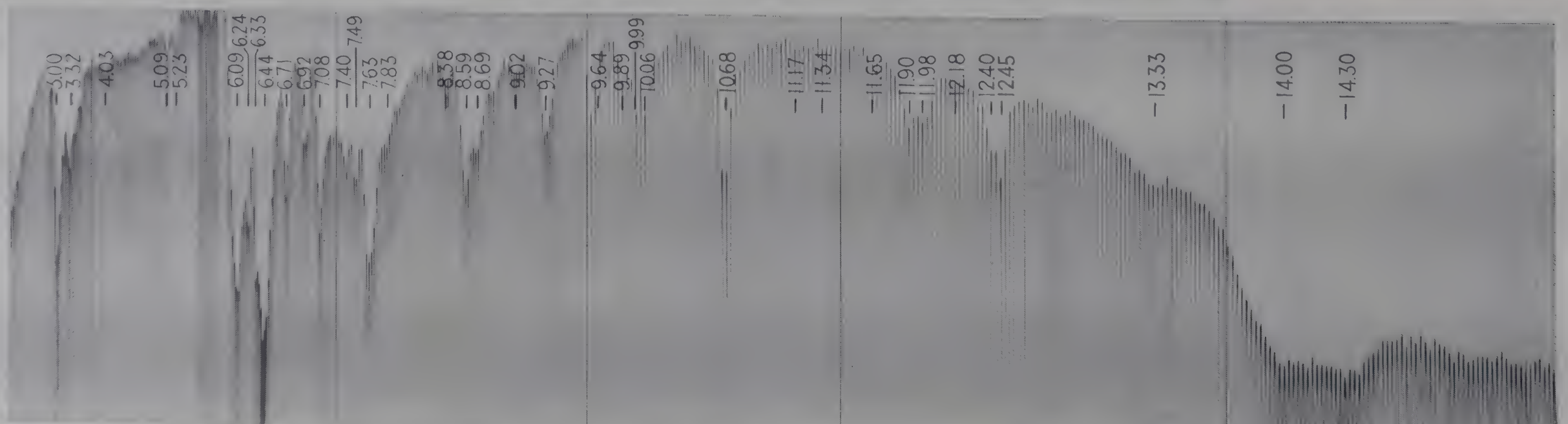


PLATE 130. 6.09 μ Amide I; 6.40 μ Amide II; 6.23 μ, 6.69 μ Phenyl. Dep. from CCl_4



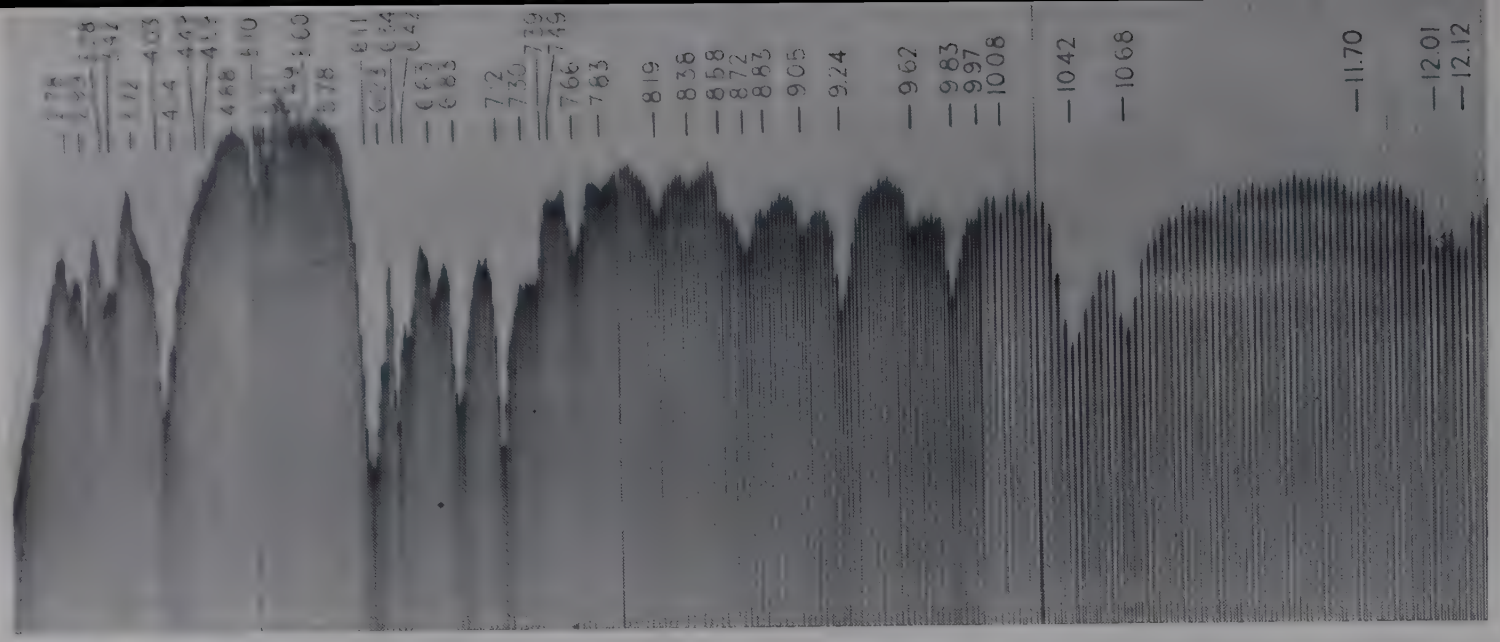


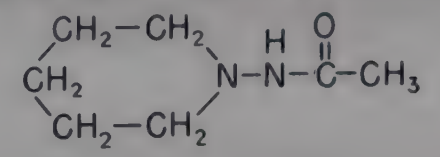
PLATE 133. Assignments: 6.11 μ Amide I
6.42 μ Residual amide II
6.23 μ, 6.34 μ, 6.63 μ Conjugated phenyl
6.83 μ Amide II (deuterized)

Preparations: Deposited from CH_3OD and D_2O

DEUTERO N-METHYL-

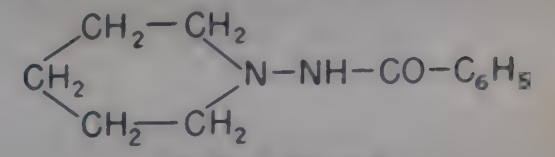
(Top)

N-ACETAMIDOPIPERIDINE



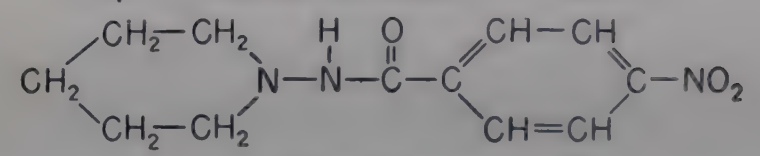
(Bottom Left)

N-BENZAMIDOPIPERIDINE



(Bottom Center)

N-p-NITROBENZAMIDOPIPERIDINE



(Bottom Right)

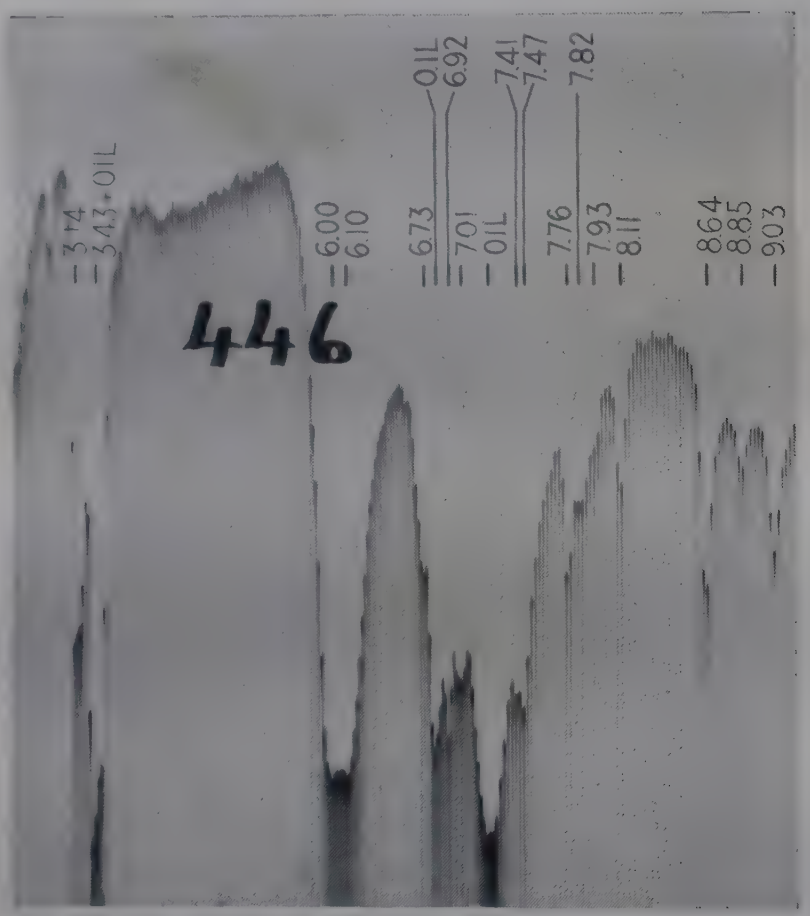


PLATE 134. Preparations: Oil paste

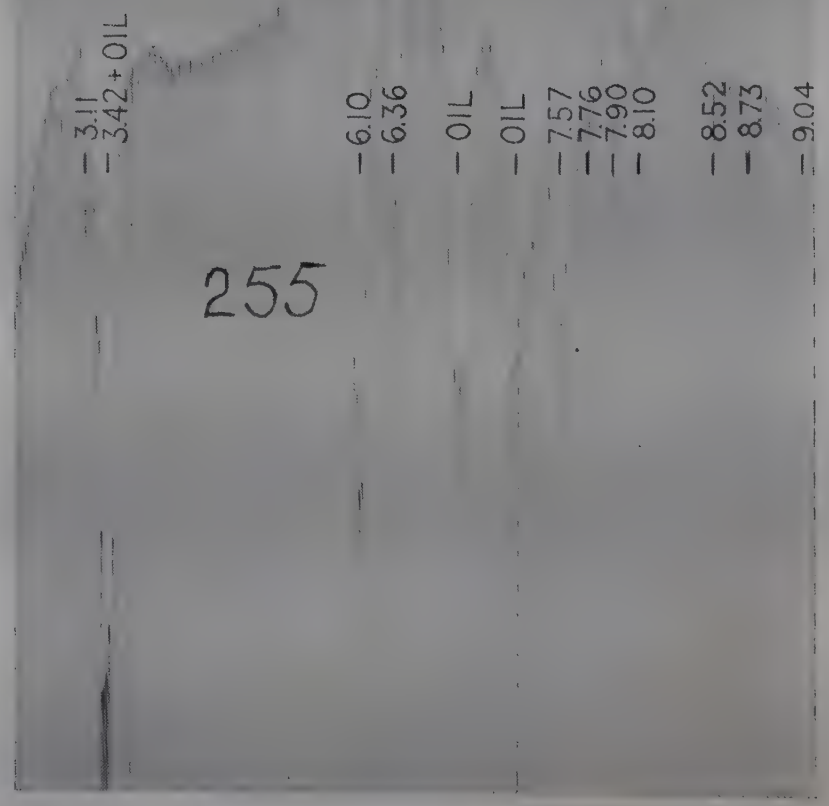


PLATE 135. Assignments: 6.10 μ Amide I
6.36 μ Amide II
Preparations: Oil paste

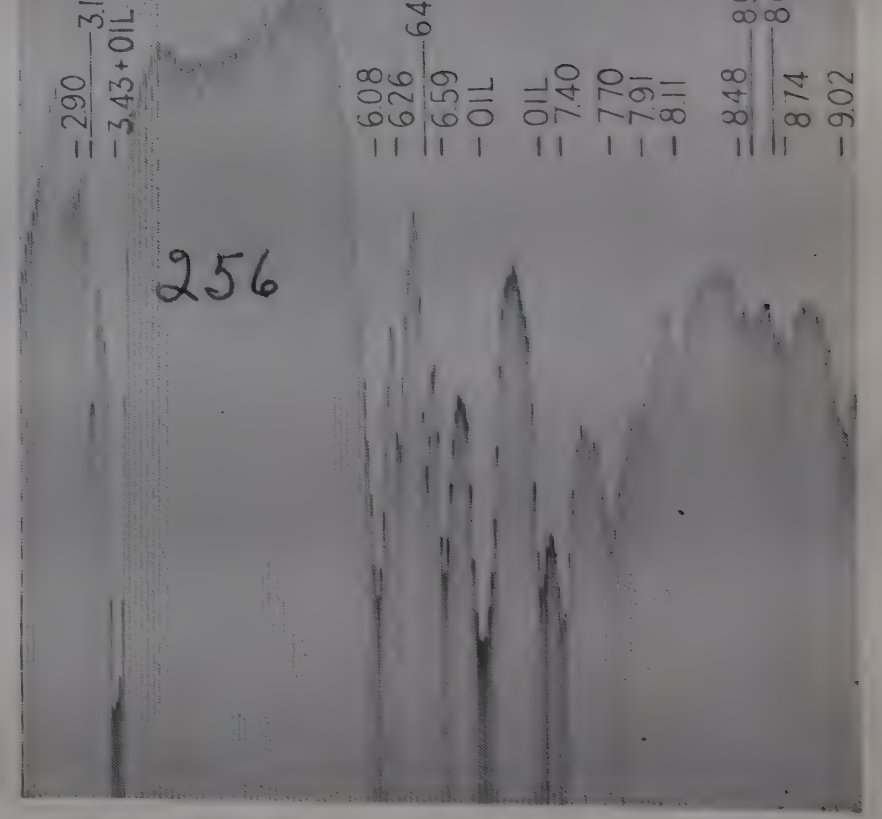


PLATE 136. Assignments: 6.08 μ Amide I
6.26 μ Unassigned
6.46 μ NO_2
6.59 μ Amide II
Preparations: Oil paste

PHENACETAMIDOALLYLMALONIC ACID

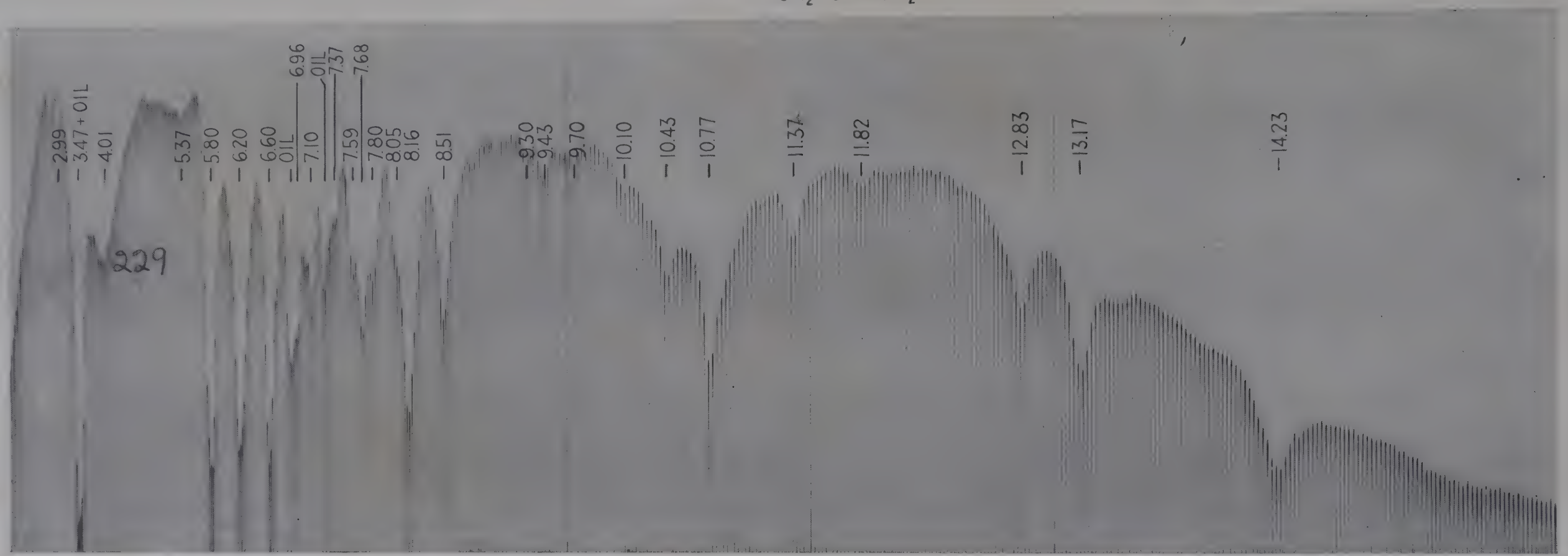
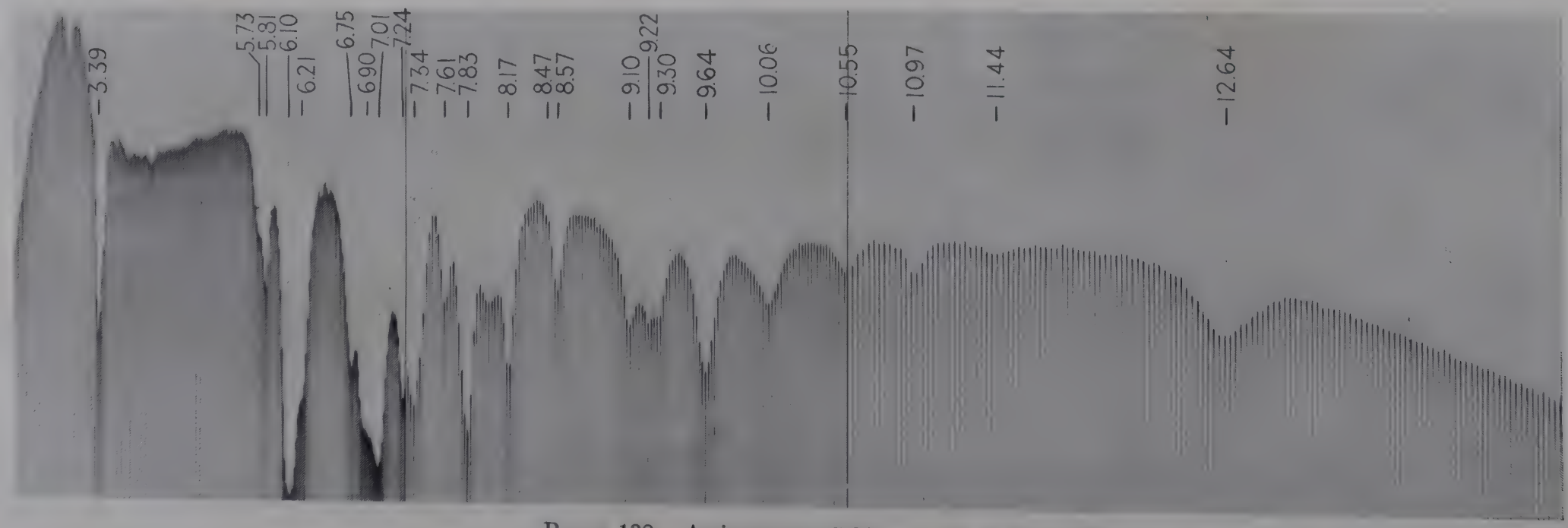
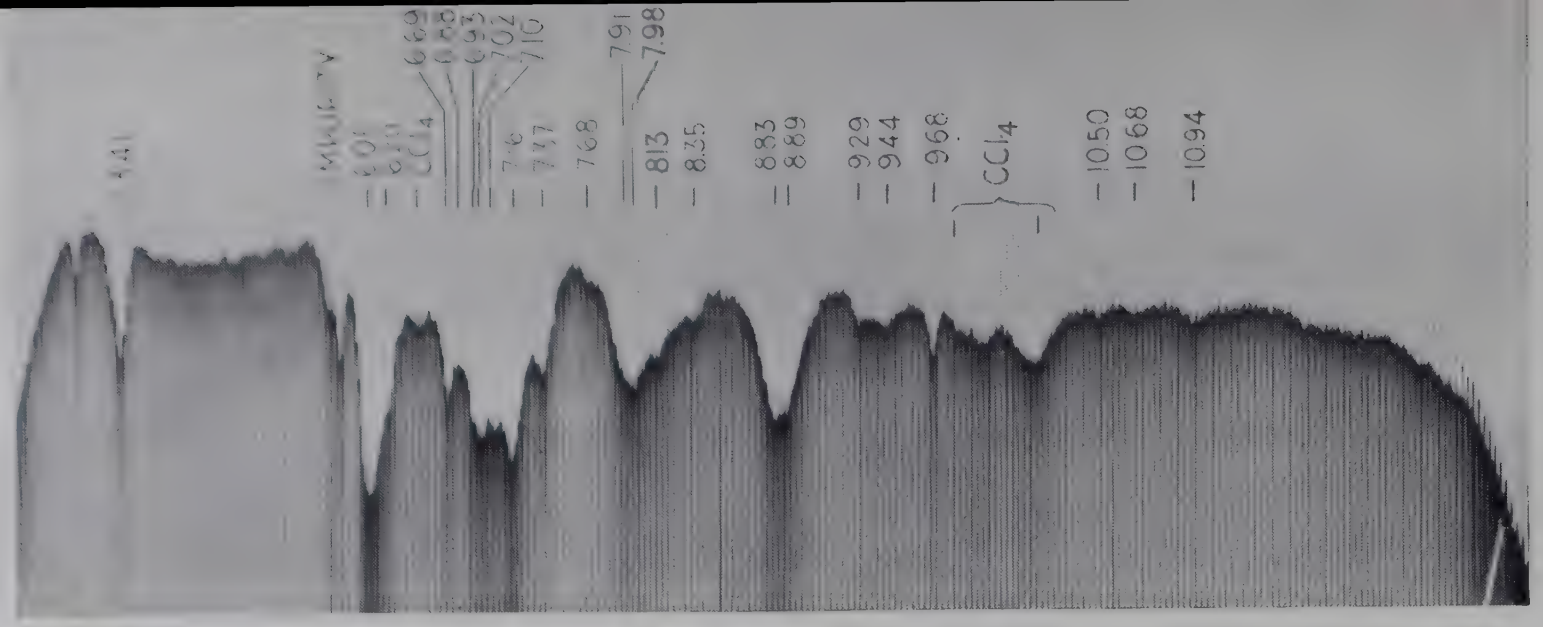


PLATE 137. Assignments: 5.80 μ Acid C=O Preparations: Deposited from pyridine
6.20 μ Amide I
6.60 μ Amide II



N,N-DIETHYLACETAMIDE

PLATE 138. Assignments: 5.81 μ Impurity Preparations: 0.005 mm.
6.10 μ Amide I



$$C_6H_5-CH_2-\overset{O}{\overset{\|}{C}}-N\begin{matrix}CH_3\\CH_3\end{matrix}$$

(Top and Center)

N,N-DIMETHYLBENZAMIDE

$$C_6H_5-\overset{O}{\overset{\|}{C}}-N\begin{matrix}CH_3\\CH_3\end{matrix}$$

(Bottom)

PLATE 140a. 6.05 μ Amide I C=O; 6.20 μ, 6.69 μ Phenyl. 5% solution in CCl_4, 0.04 mm.

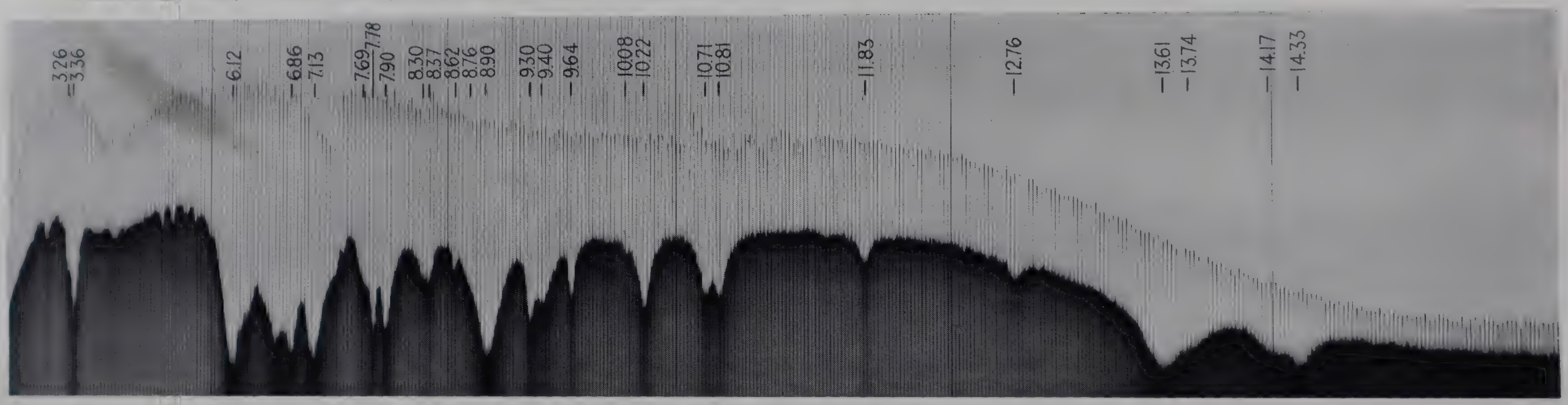


PLATE 140. Assignments: 6.12 μ Amide I Preparations: 0.015 mm.

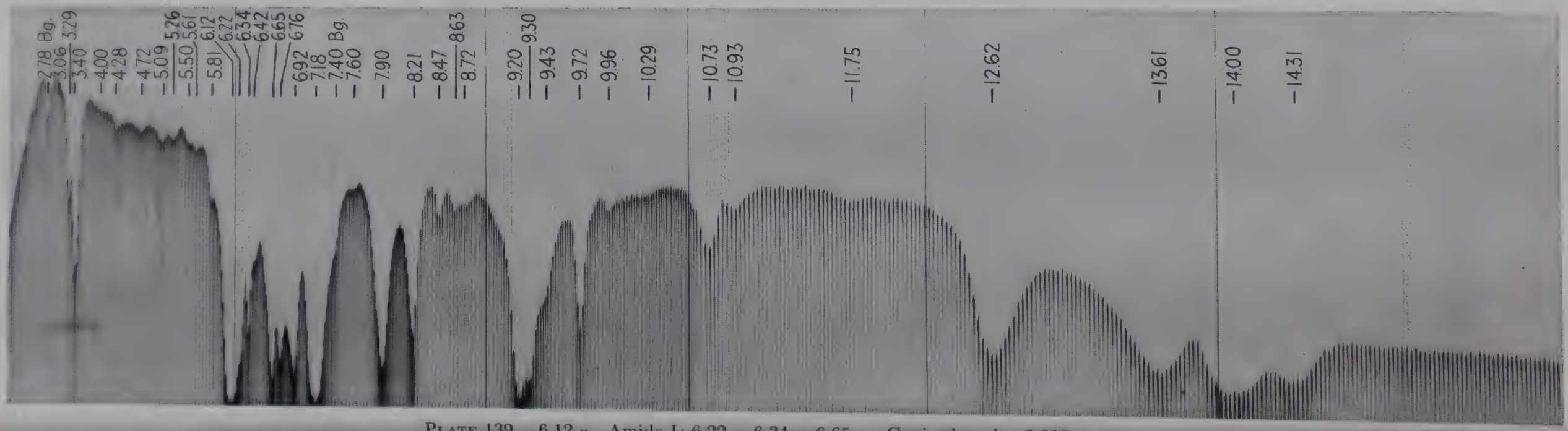
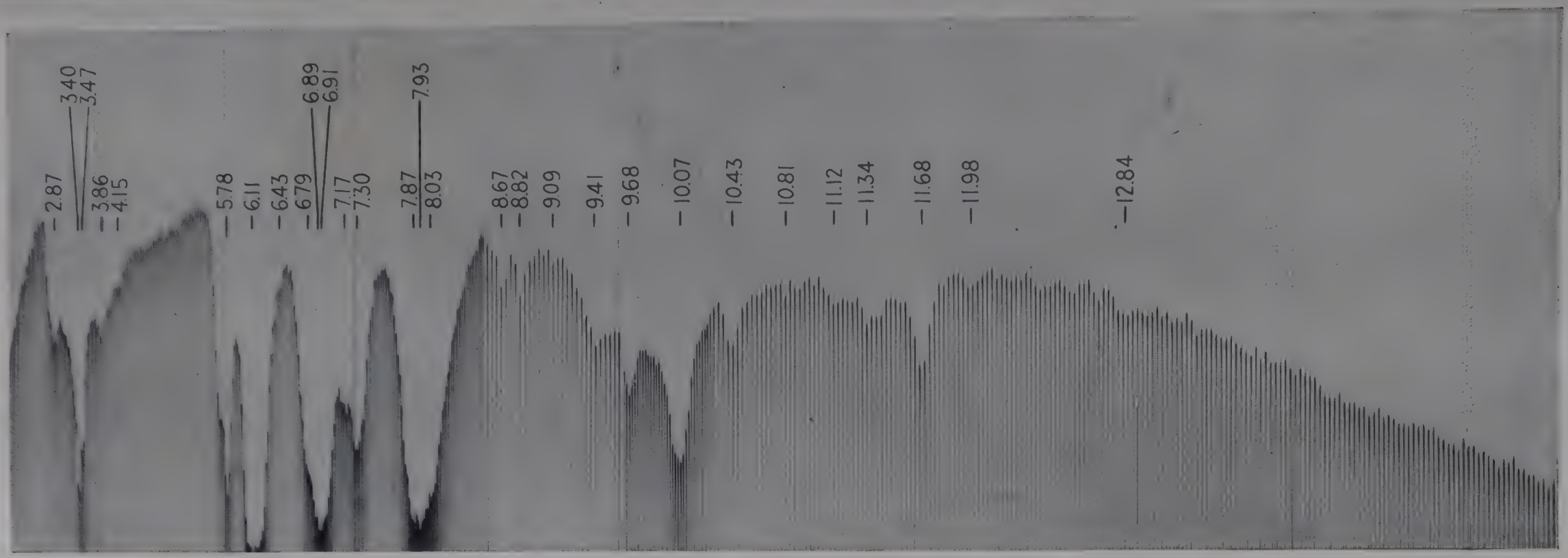
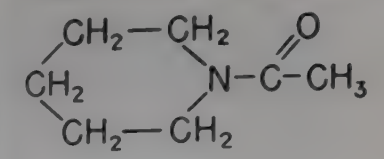


PLATE 139. 6.12 μ Amide I; 6.22 μ, 6.34 μ, 6.65 μ Coni. phenyl. 0.015 mm.

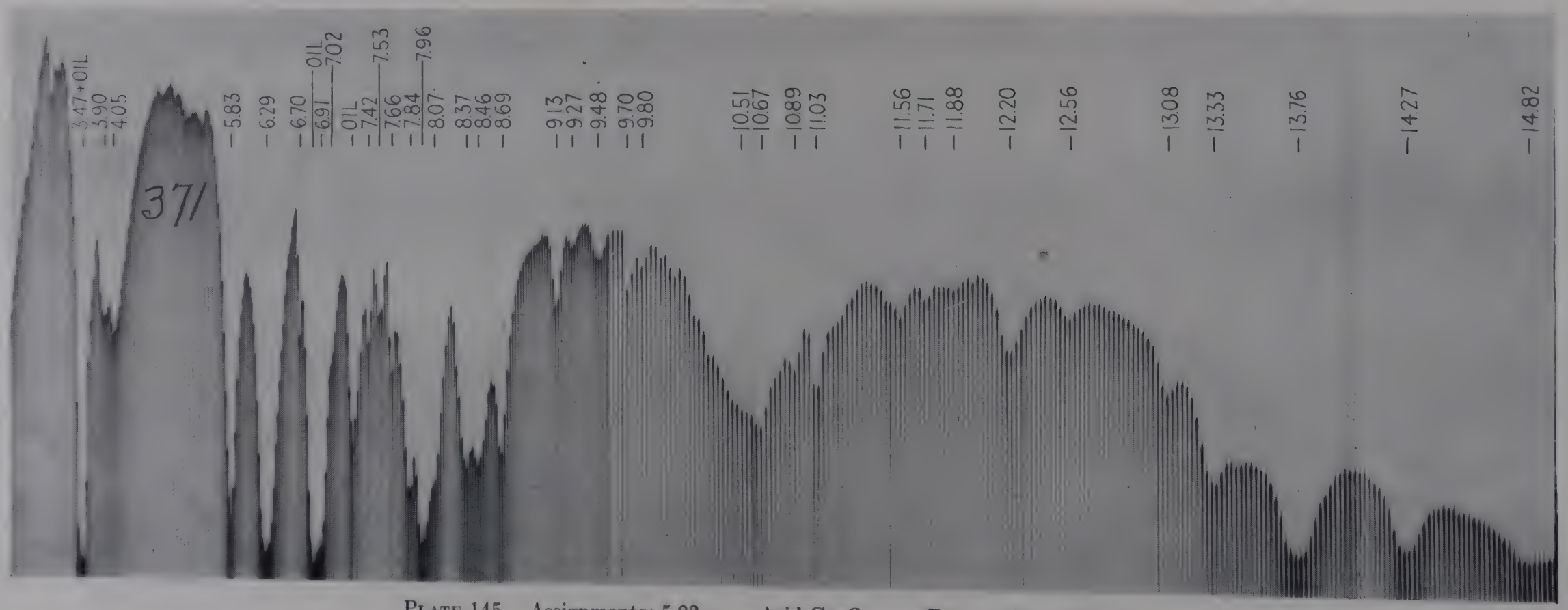


ACETYL PIPERIDINE



(impure)

PLATE 141. Assignments: 5.78 μ Acetic acid Preparations: 0.005 mm.
6.11 μ N-acyl C=O



L-N-PHENACETYLPROLINE

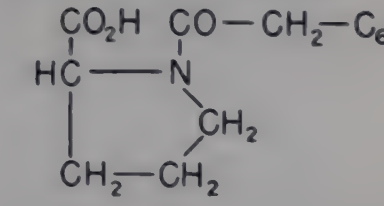


PLATE 145. Assignments: 5.83 μ Acid C=O Preparations: Oil paste
6.29 μ N-acyl C=O

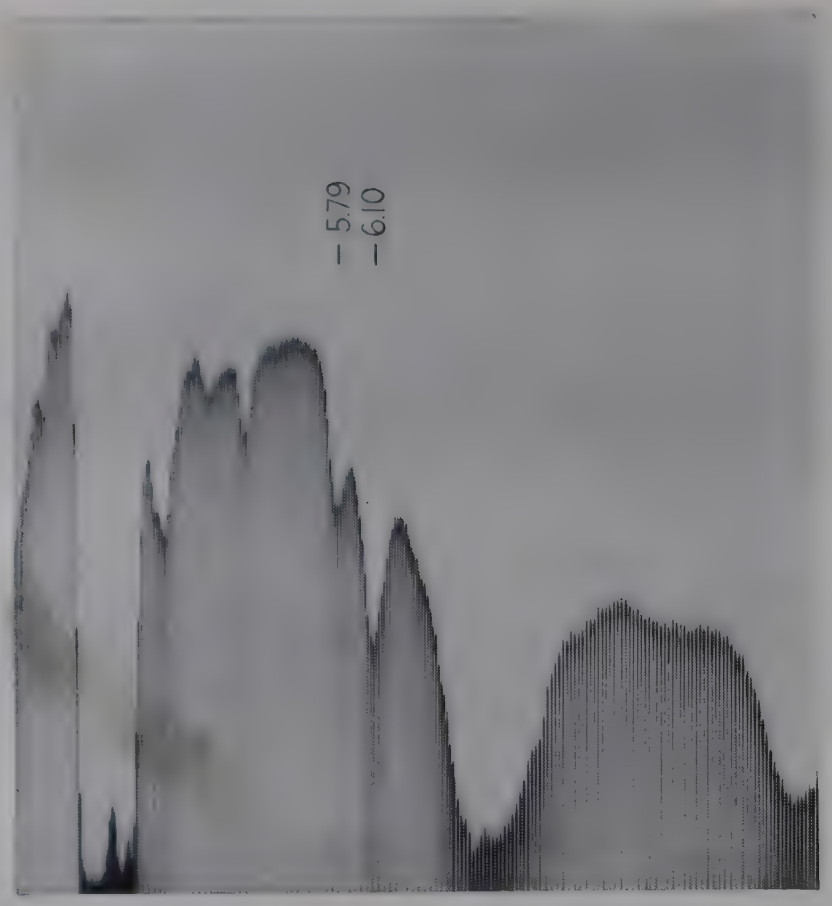
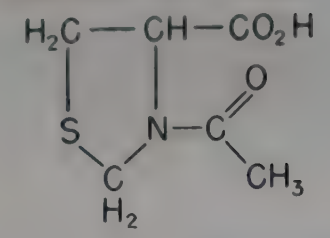


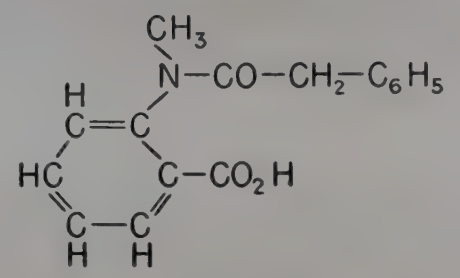
PLATE 142a. Assignments: 5.79 μ Acid C=O
6.10 μ N-acyl C=O
Preparations: Methanol solution 0.02 mm.

N-ACETYLTHIAZOLIDINE-4-CARBOXYLIC ACID



(Top Left and Bottom)

N-PHENACETYL-N-METHYL ANTHRANILIC ACID



(Top Right)

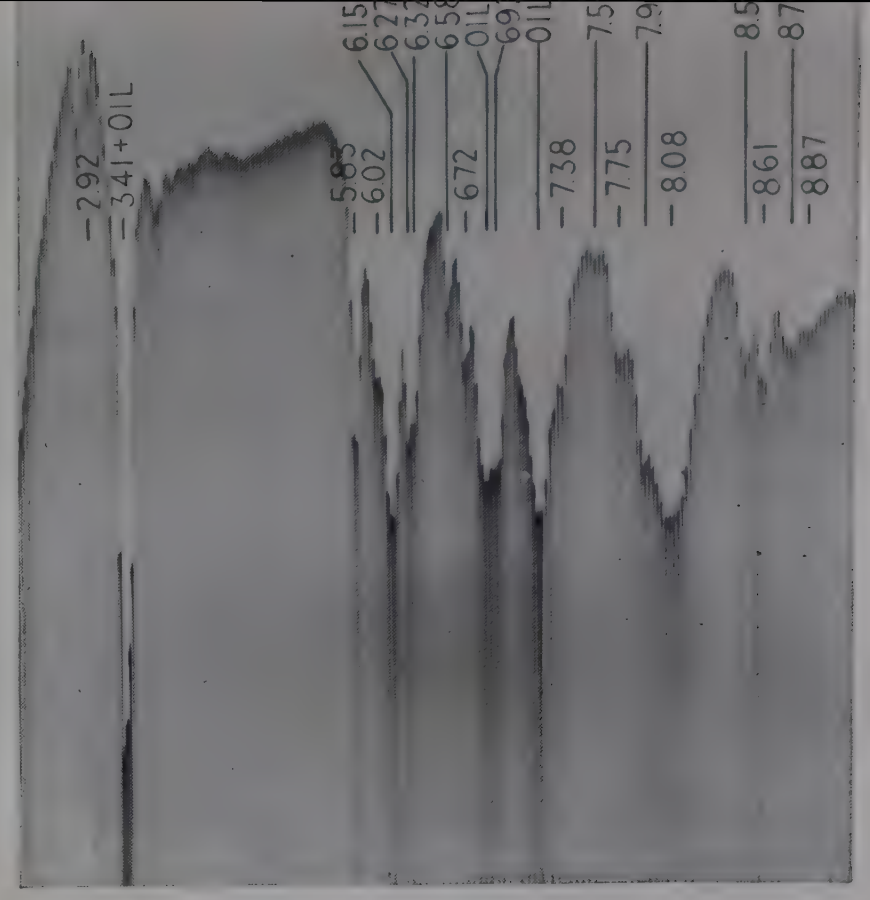


PLATE 143. Assignments: 5.83 μ Acid C=O
6.15 μ Amide I
6.27 μ, 6.32 μ, 6.72 μ Conjugated phenyl
Preparations: Oil paste

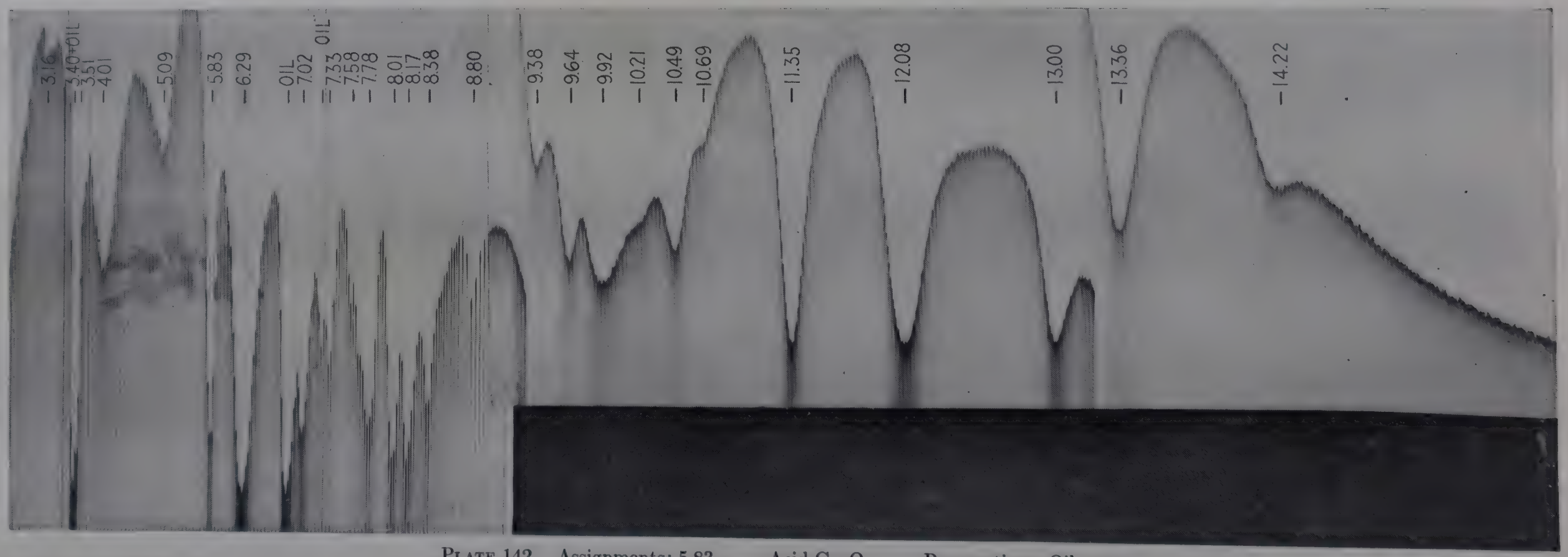


PLATE 142. Assignments: 5.83 μ Acid C=O
6.29 μ N-acyl C=O
Preparations: Oil paste

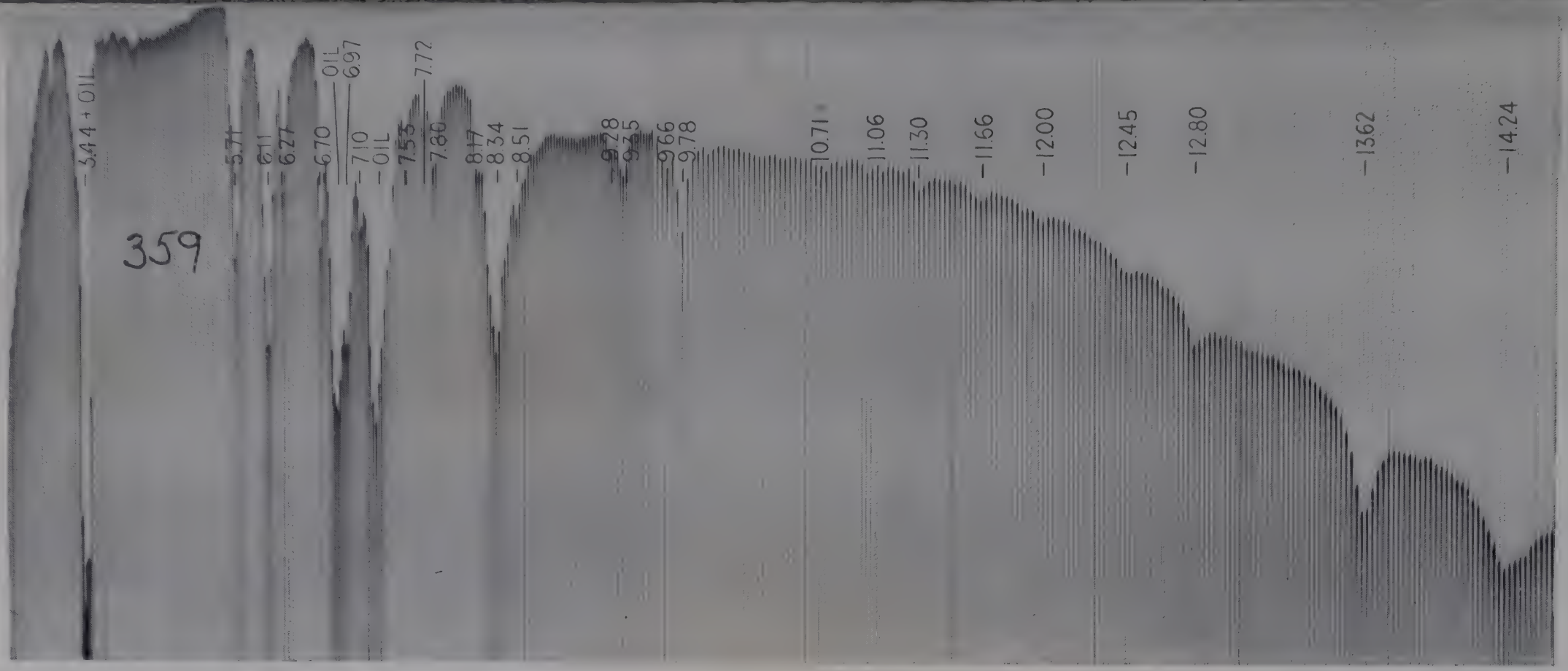


PLATE 146. Assignments: 5.71 μ Acid C=O; 6.11 μ Amide I; 6.27 μ, 6.70 μ Phenyl. Preparations: Oil paste

N-PHENACETYL-N-PHENYLGLYCINE

$CH_2\text{-}CO_2H$
|
$N\text{-}CO\text{-}CH_2\text{-}C_6H_5$
|
C_6H_5

N-PHENACETYL-N-PHENYLGLYCINE
METHYL ESTER

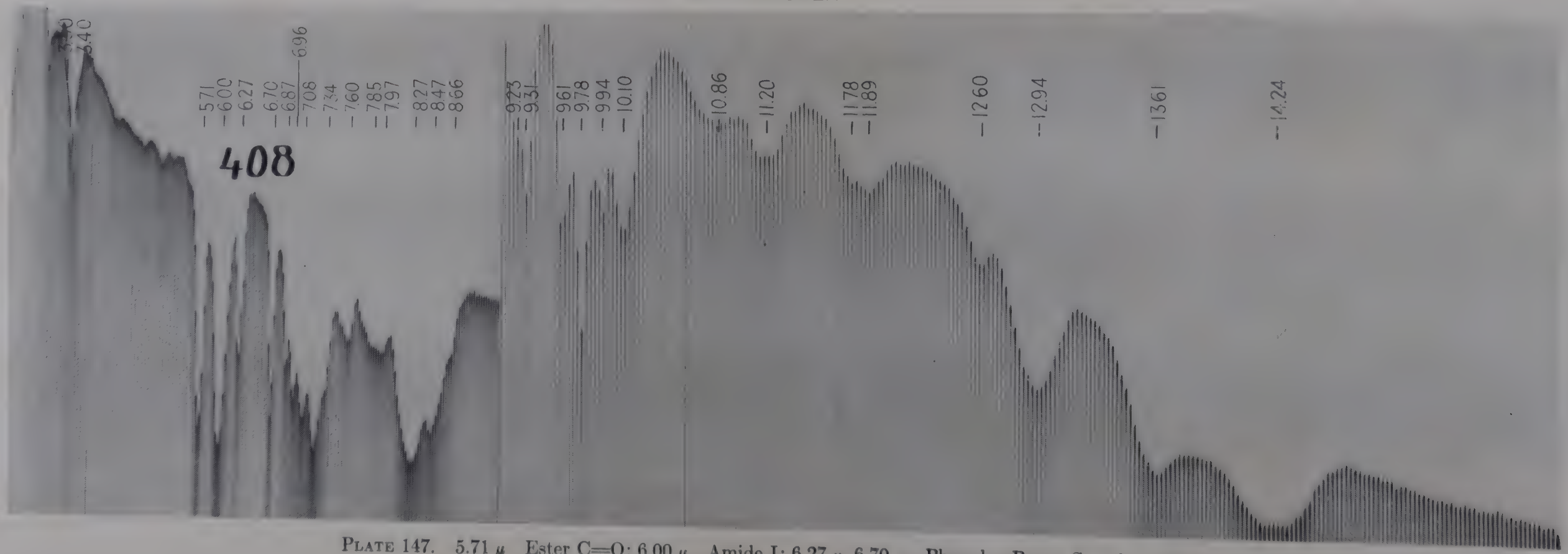


PLATE 147. 5.71 μ Ester C=O; 6.00 μ Amide I; 6.27 μ, 6.70 μ Phenyl. Prep.: See plate 149

N-PHENACETYLSARCOSINE

$$C_6H_5-CH_2-CO-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2-CO_2H$$

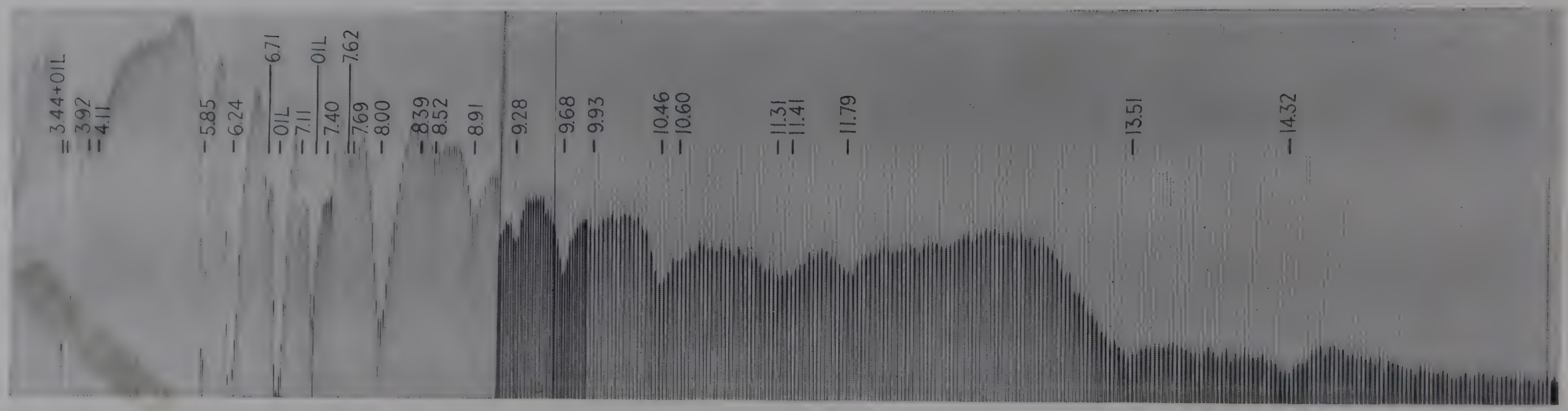


PLATE 148. Assignments: 5.85 μ Acid C=O Preparations: 2–9 μ oil paste
6.24 μ Amide I 9–15 μ deposited from acetone

N-PHENACETYLSARCOSINE METHYL ESTER

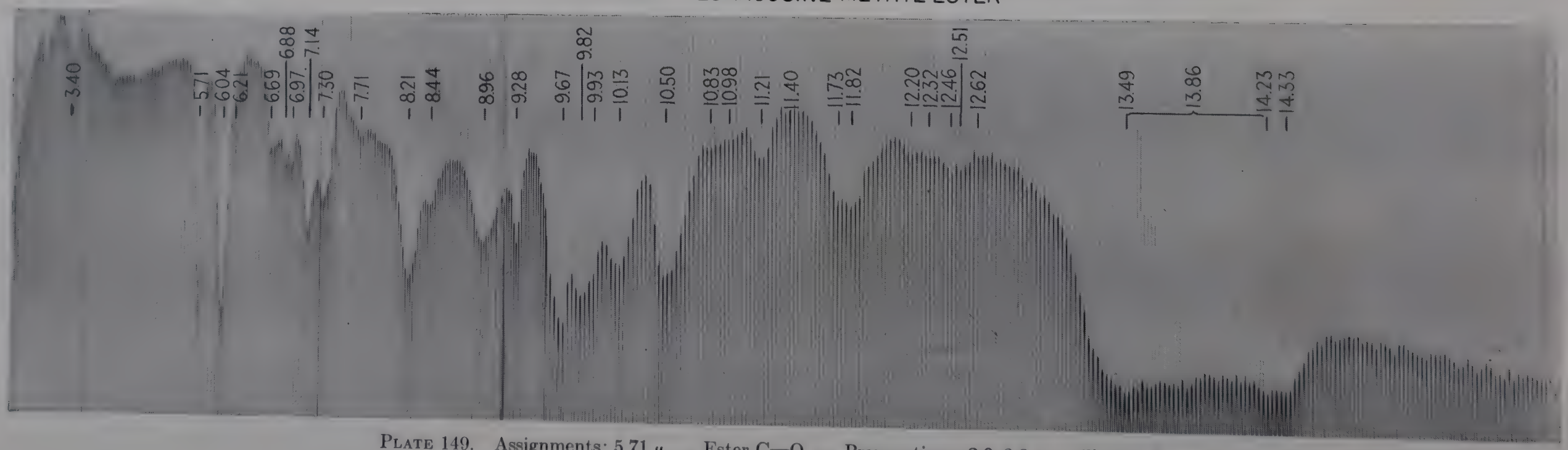


PLATE 149. Assignments: 5.71 μ Ester C=O Preparations: 2.0–9.0 μ capillary cell
6.04 μ Amide I 9.0–15 μ, 0.02 mm.
6.21 μ, 6.69 μ Phenyl

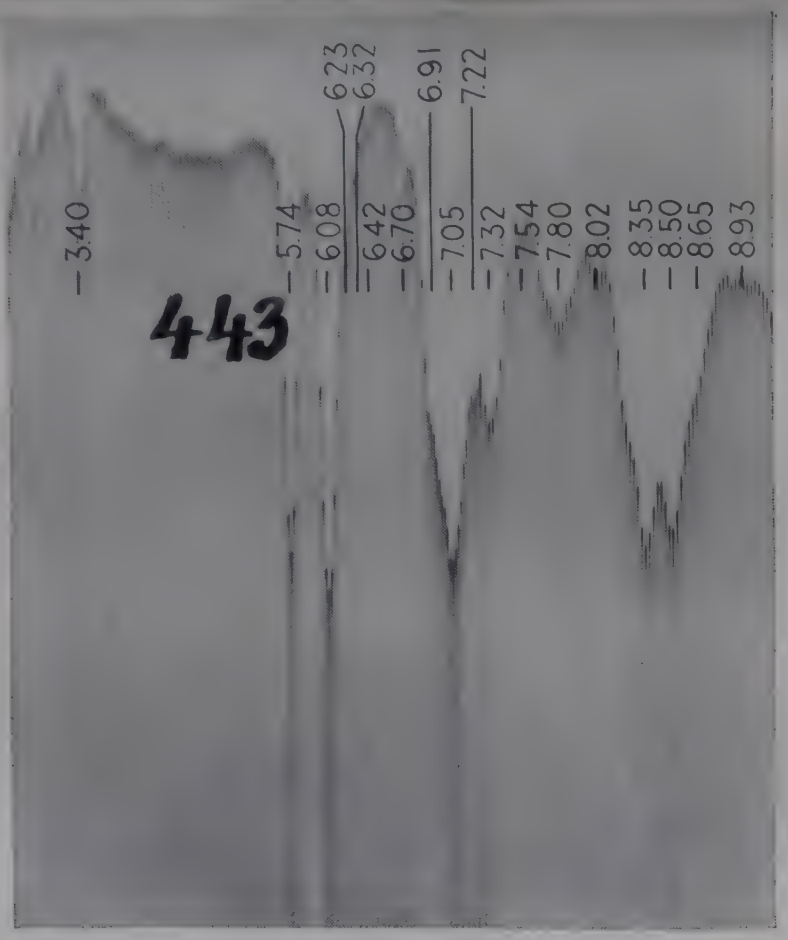


PLATE 144. Assignments: 5.74 μ Ester C=O
6.08 μ N-acyl C=O
Preparations: Capillary cell

l-N-PHENACETYLPROLINE
METHYL ESTER
(Top Left)

URETHANE

$$NH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5$$

(Top Right)

N,N'-DIMETHYL-N-BENZOYLBENZAMIDINE

$$C_6H_5-\overset{\overset{N-CH_3}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}-\overset{\overset{O}{\|}}{C}-C_6H_5$$

(Bottom)

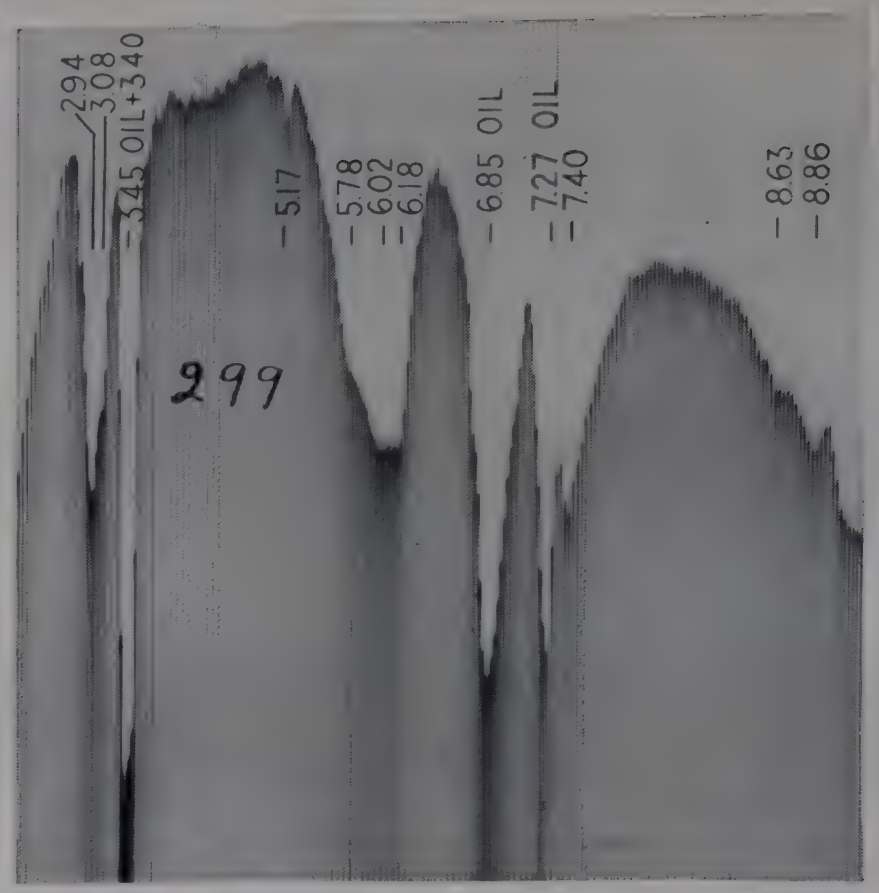


PLATE 151. Assignments:
6.02 μ Joint ester-amide C=O
6.18 μ NH_2
Preparations: Oil paste

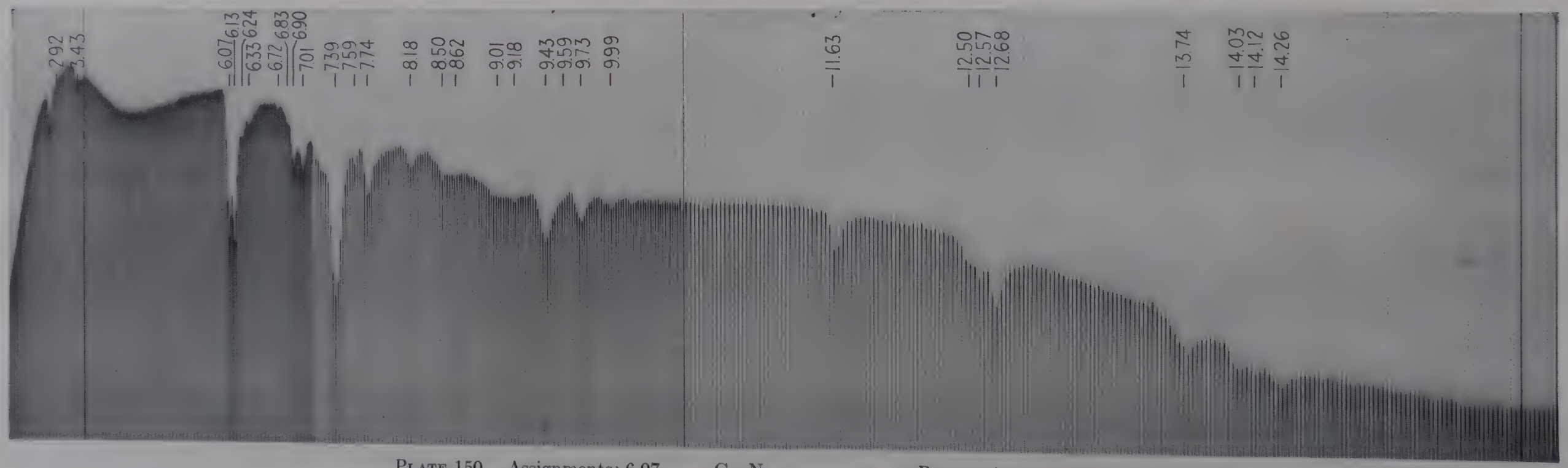


PLATE 150. Assignments: 6.07 μ C=N
6.13 μ N-acyl C=O
6.24 μ, 6.33 μ, 6.71 μ Conjugated phenyl
Preparations: 0.015 mm.

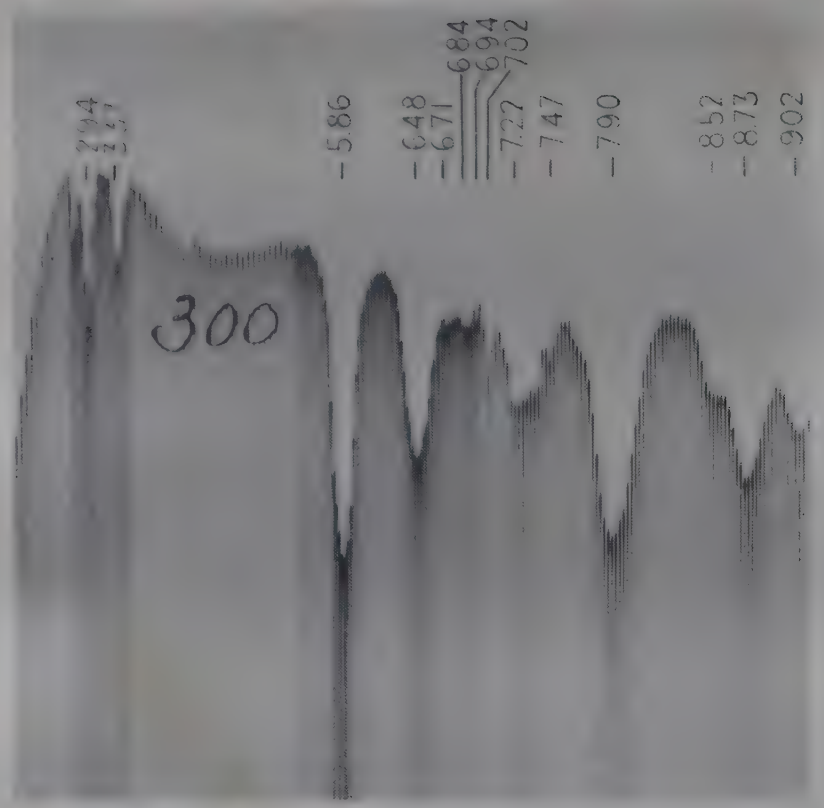
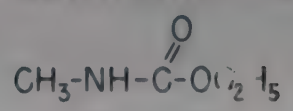


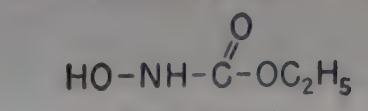
PLATE 152. Assignments:
5.86 μ Joint ester-amide C=O
6.48 μ Amide II
Preparations: 0.02 mm.

N-METHYLURETHANE



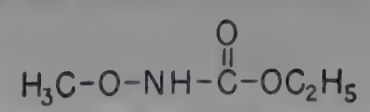
(*Top Left*)

N-HYDROXYURETHANE



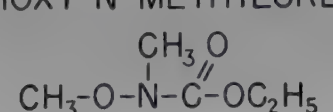
(*Top Right*)

N-METHOXYURETHANE



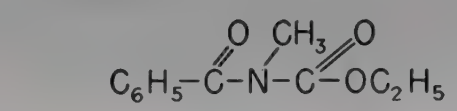
(*Bottom Left*)

N-METHOXY-N-METHYLURETHANE



(*Bottom Center*)

N-BENZOYL-N-METHYLURETHANE



(*Bottom Right*)

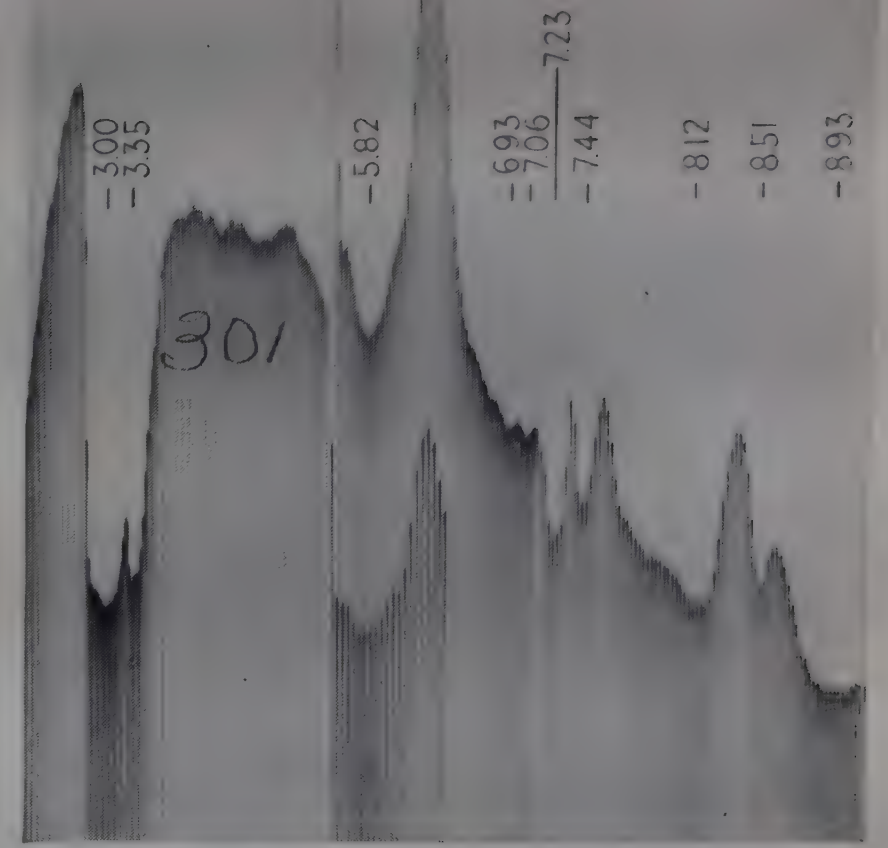


PLATE 153. Assignments:
5.82 μ Joint ester-amide C=O
Preparations: Capillary cell

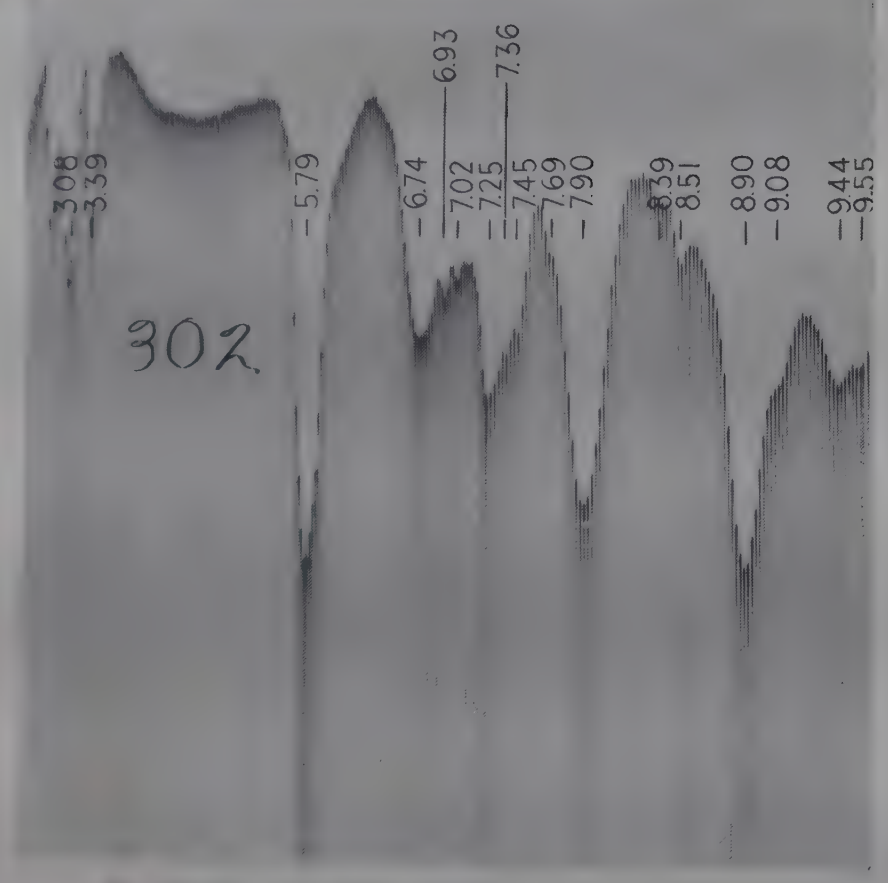


PLATE 154. Assignments:
5.79 μ Joint ester-amide C=O
Preparations: Capillary cell

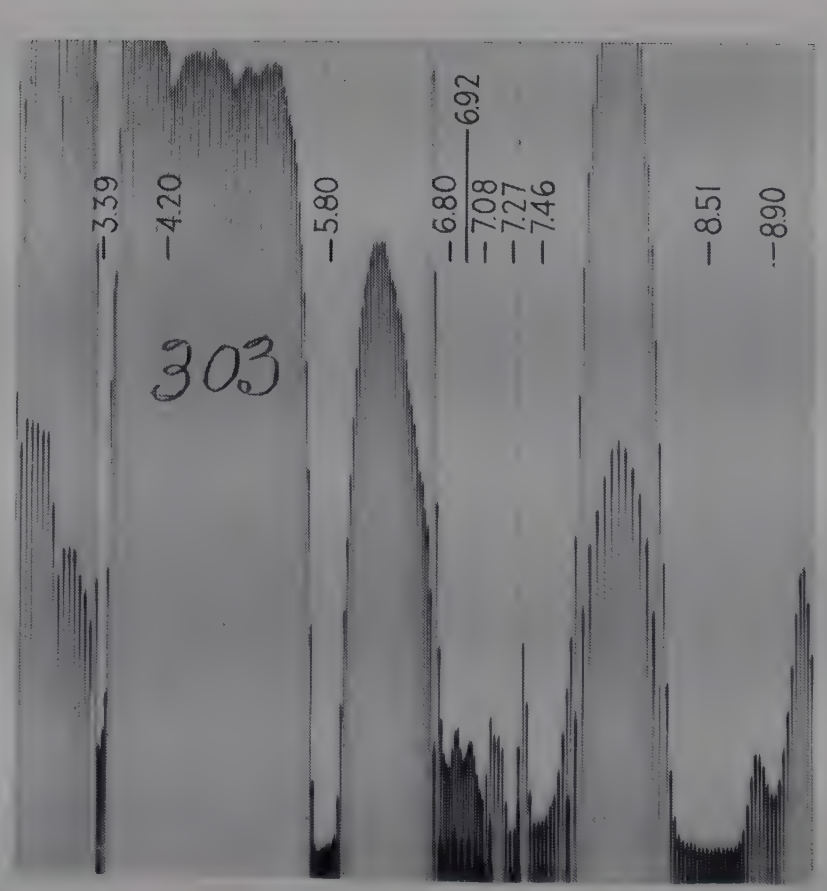


PLATE 155. Assignments:
5.80 μ Joint ester-amide C=O
Preparations: 0.02 mm.

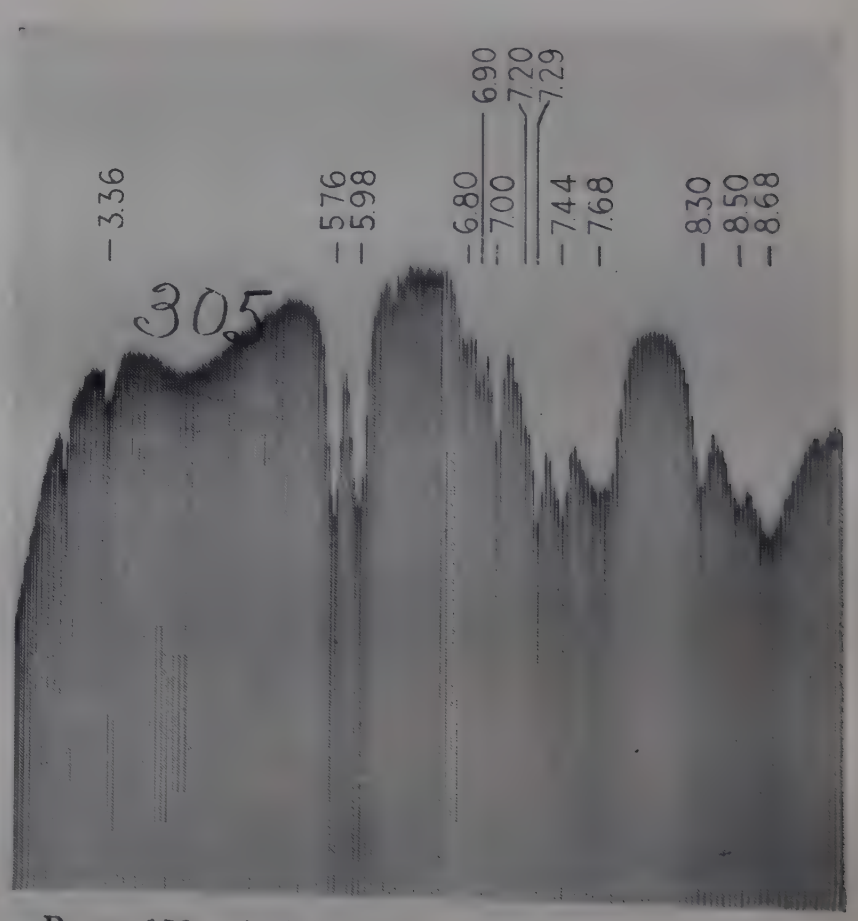


PLATE 156. Assignments:
5.76 μ Joint ester-amide C=O
5.98 μ N-acyl C=O (conjugated)

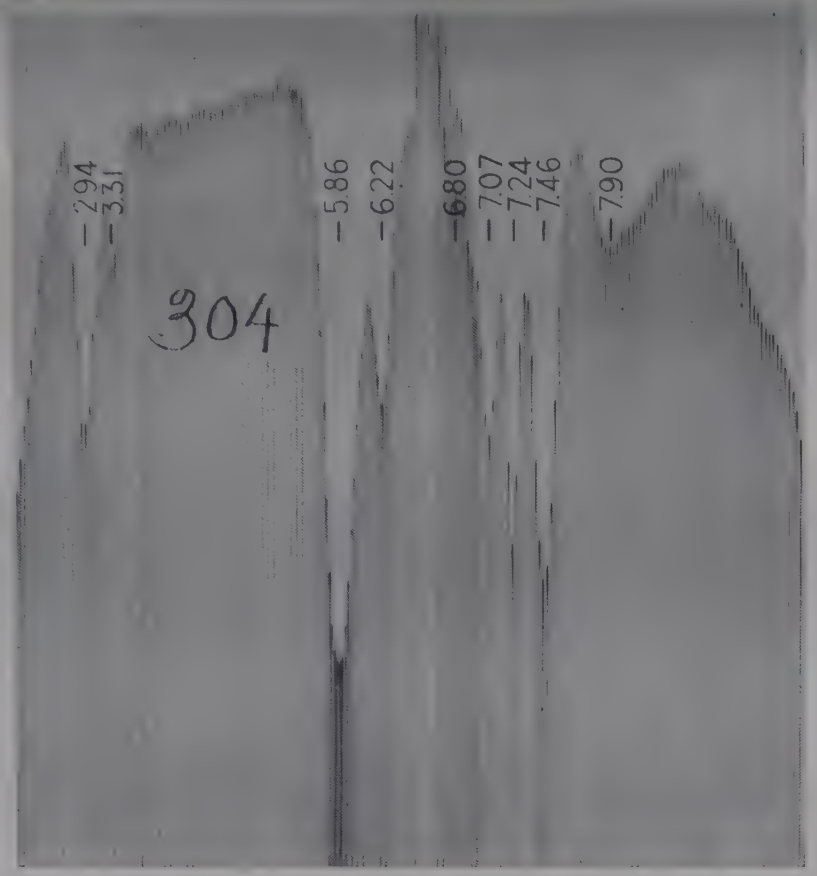
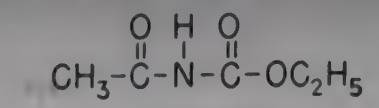


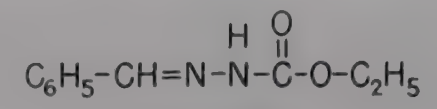
PLATE 157. Assignments: 5.86 μ C=O conjugated
Preparations: Capillary cell
(*See p.* 12)

ACETYL URETHANE



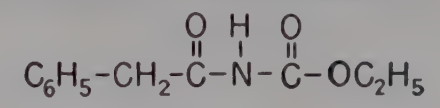
(*Top Left*)

N-CARBETHOXYBENZALHYDRAZONE



(*Top Right*)

PHENACETYL URETHANE



(*Bottom*)

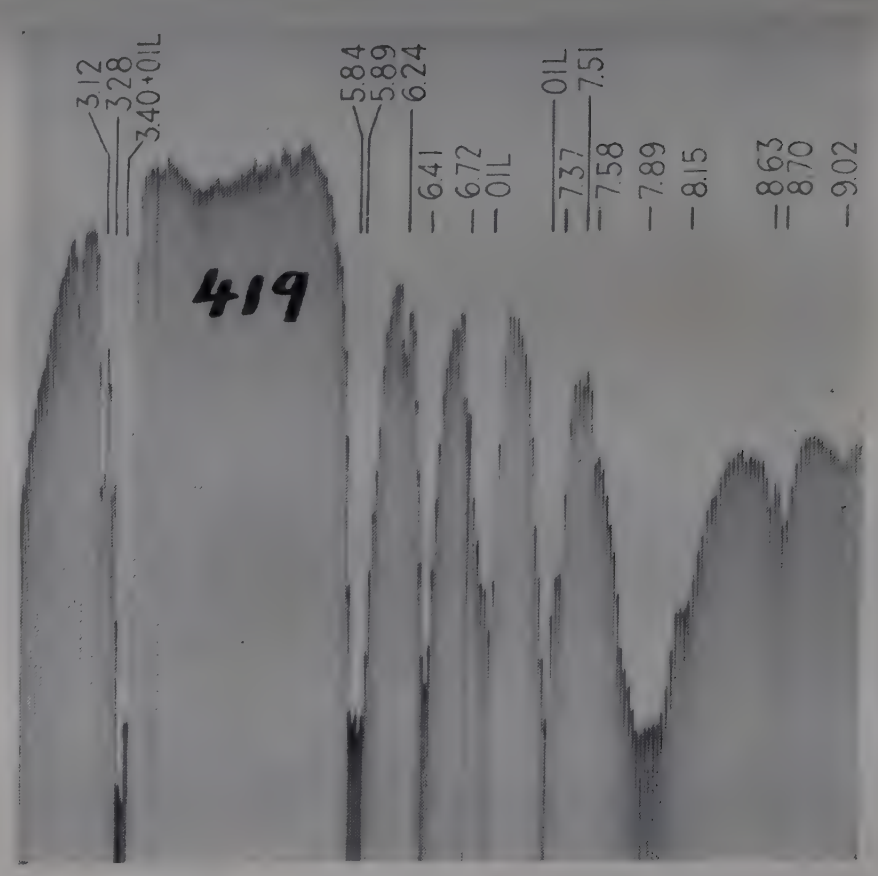


PLATE 159. Assignments:
5.84 μ Joint ester-amide C=O
5.89 μ C=N
6.41 μ Amide II
Preparations: Oil paste

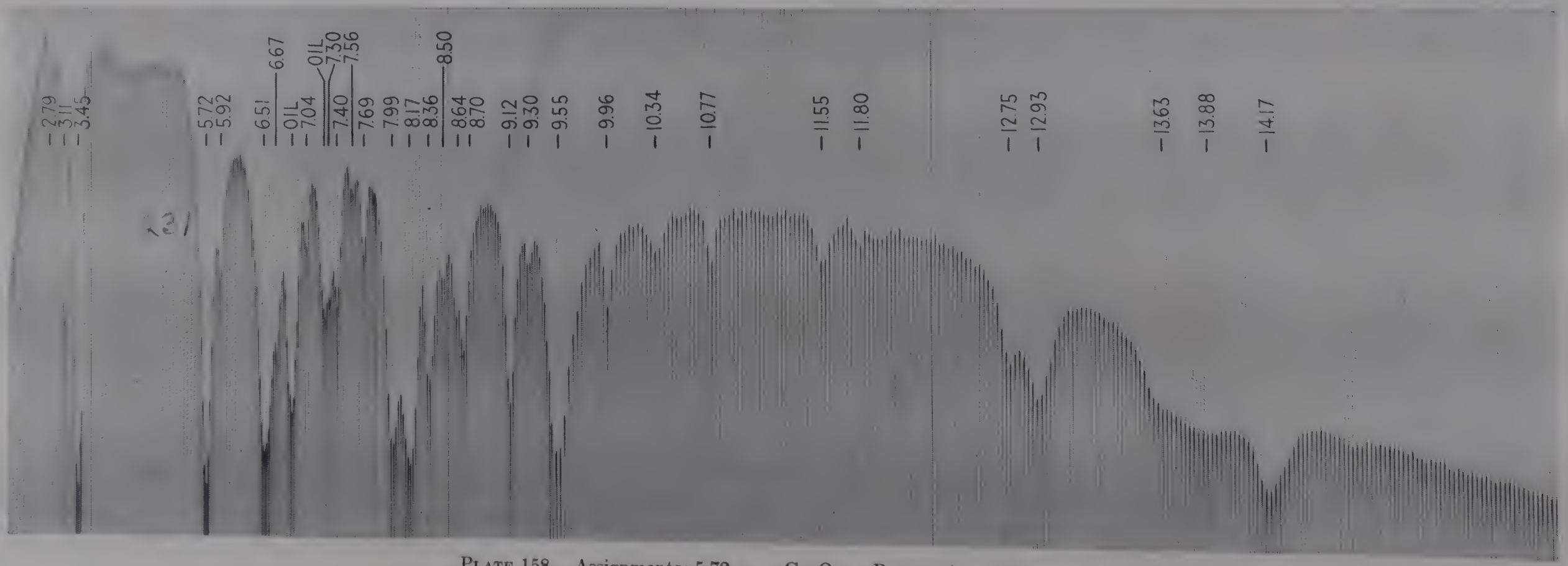


PLATE 158. Assignments: 5.72 μ C=O Preparations: Oil paste

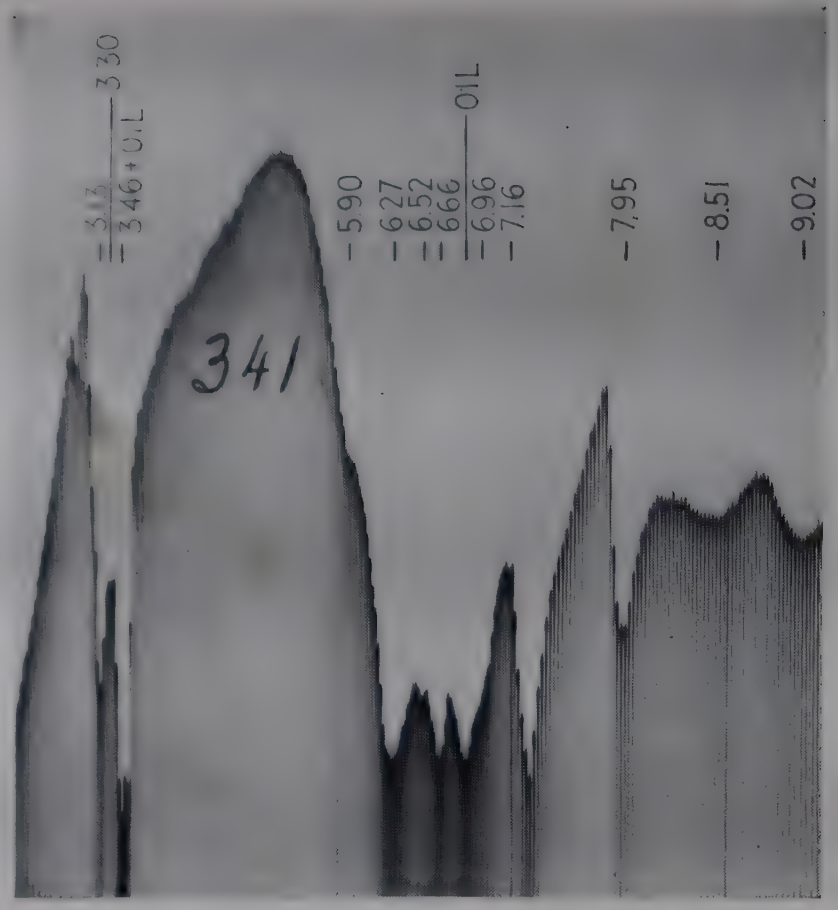


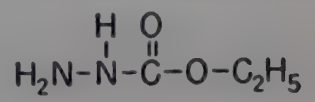
PLATE 161. Assignments: 6.27 μ Amide I
6.52 μ Amide II
Preparations: Oil paste

1,2-DIACETYLHYDRAZINE

CH_3-CO-NH-NH-CO-CH_3

(Top Left)

ETHYL CARBAZATE



(Top Right)

HYDRAZINE (ANHYDROUS)

(Bottom)

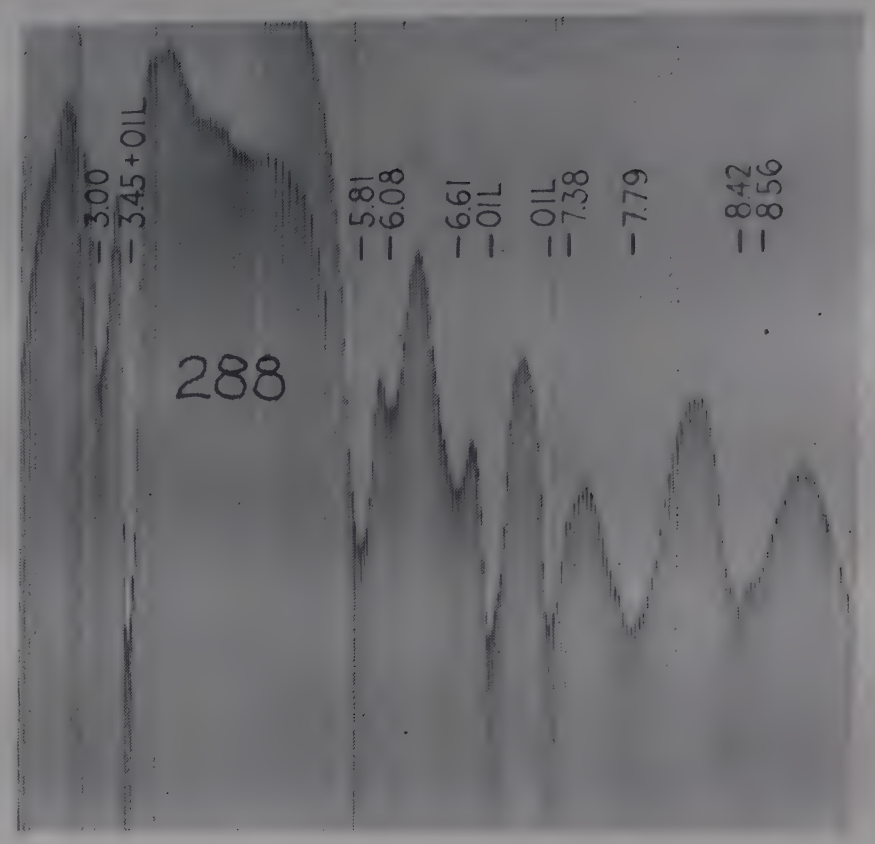


PLATE 162. Assignments:
5.81 μ Joint ester-amide C=O
6.08 μ NH_2(?)
6.61 μ Amide II
Preparations: Oil paste

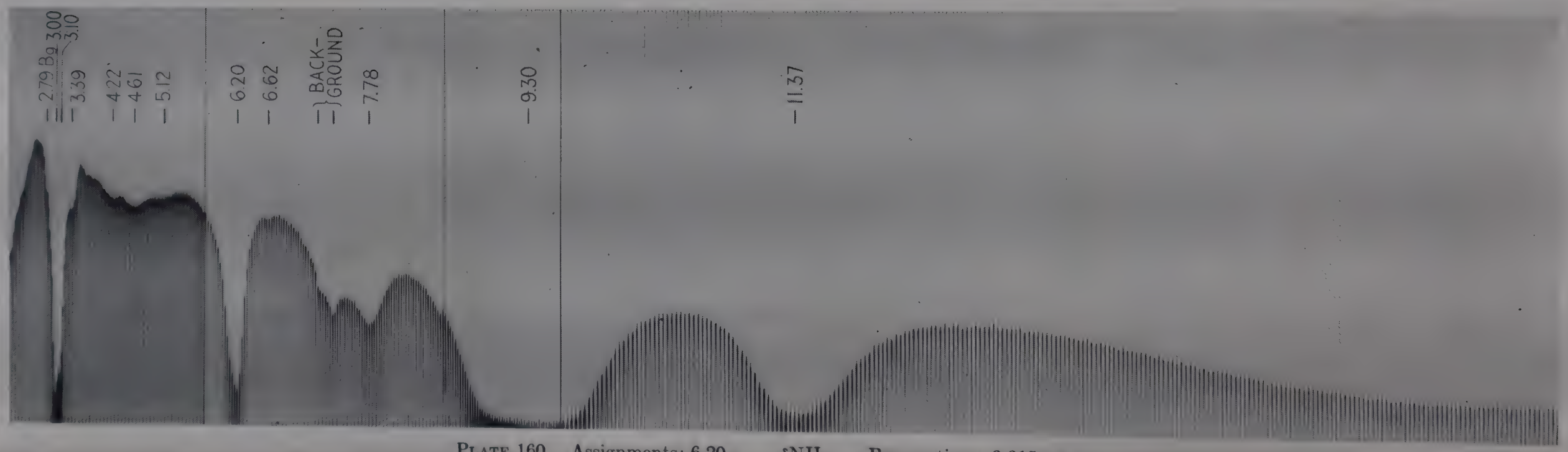


PLATE 160. Assignments: 6.20 μ δNH_2 Preparations: 0.015 mm.

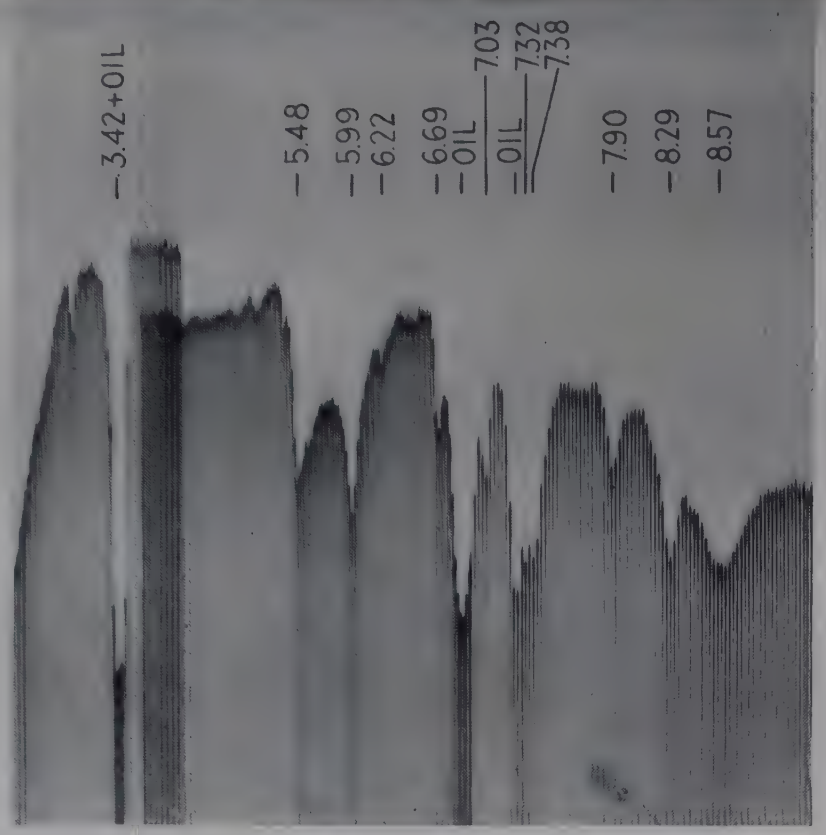
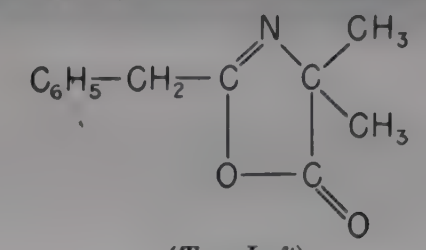


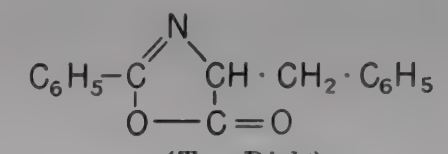
PLATE 163. Assignments: 5.48 μ C=O
5.99 μ C=N
6.22 μ, 6.69 μ Phenyl
Preparations: Oil paste

2-BENZYL-4,4-DIMETHYLOXAZOLONE-5



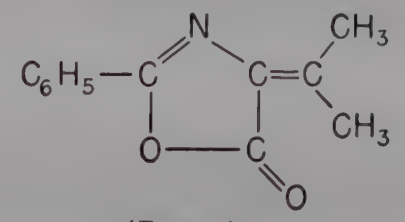
(Top Left)

2-PHENYL-4-BENZYLOXAZOLONE-5



(Top Right)

2-PHENYL-4-ISOPROPYLIDENE OXAZOLONE-5



(Bottom)

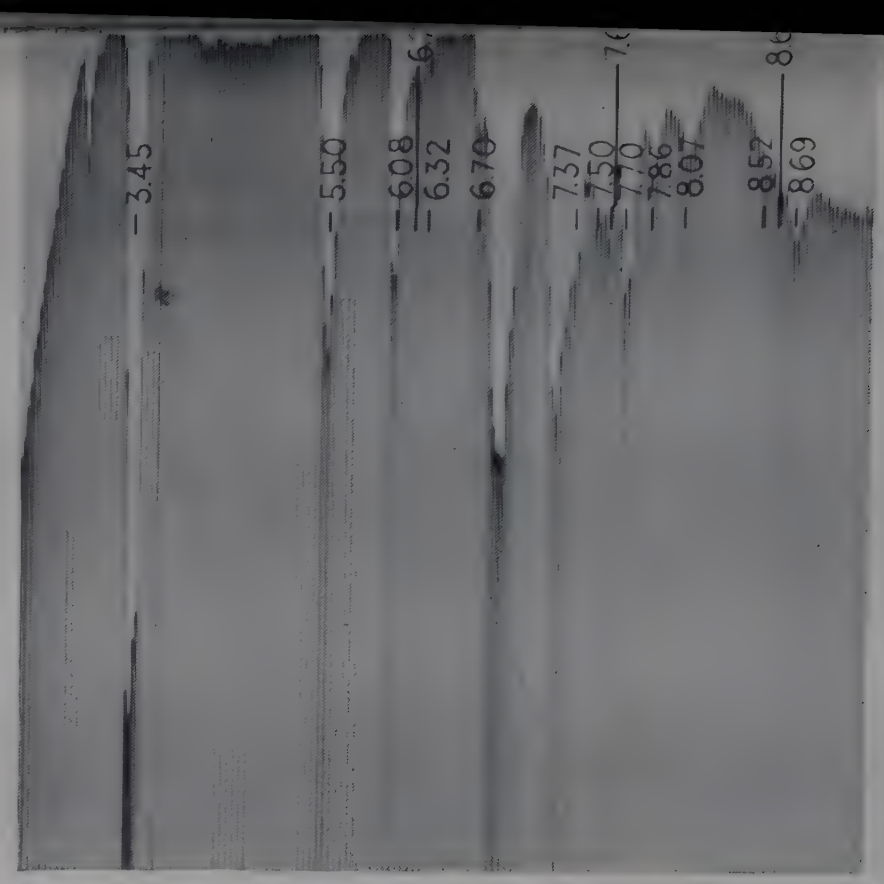


PLATE 164. Assignments: 5.50 μ C=O
6.08 μ C=N
6.22 μ, 6.32 μ, 6.70 μ Conjugated phenyl
Preparations: Oil paste

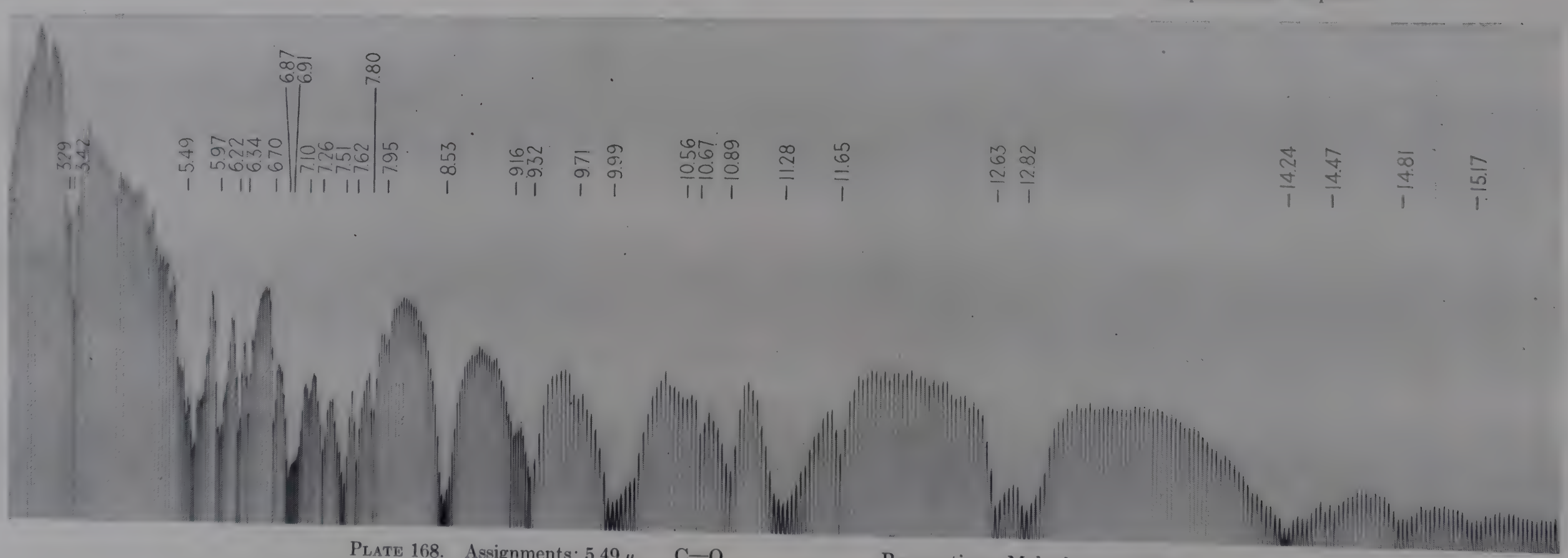


PLATE 168. Assignments: 5.49 μ C=O
5.97 μ C=N
6.22 μ, 6.34 μ, 6.70 μ Conjugated phenyl
Preparations: Melted and solidified

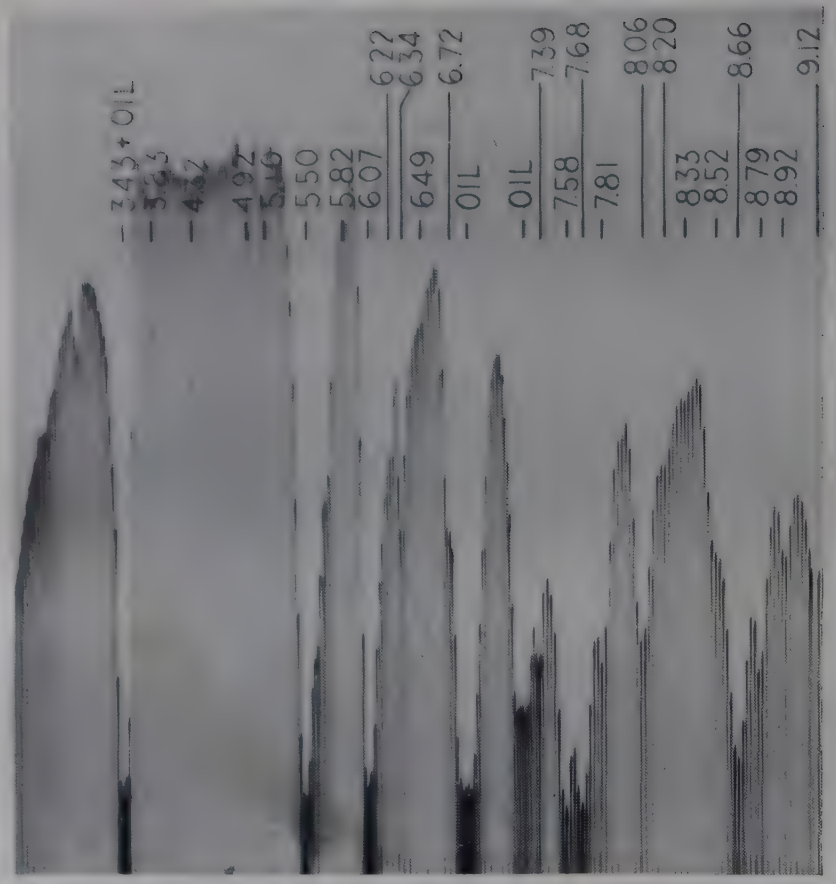
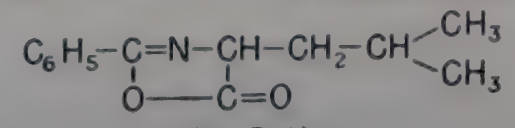


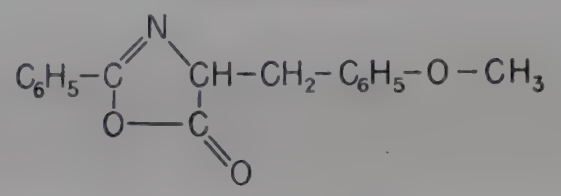
PLATE 165. Assignments: 5.50 μ C=O
6.07 μ C=N
6.22 μ, 6.34 μ, 6.72 μ } Conjugated phenyl
Preparations: Oil paste

2-PHENYL-4-ISOBUTYLOXAZOLONE-5



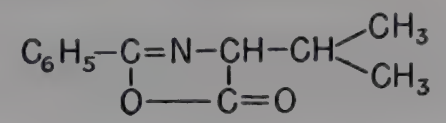
(Top Left)

2-PHENYL-4-(P-METHOXY BENZYL) OXAZOLONE-5



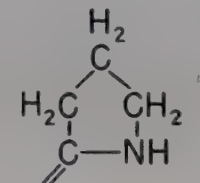
(Top Right)

2-PHENYL-4-ISOPROPYLOXAZOLONE-5



(Bottom Left)

γ-BUTYROLACTAM



(Bottom Right)

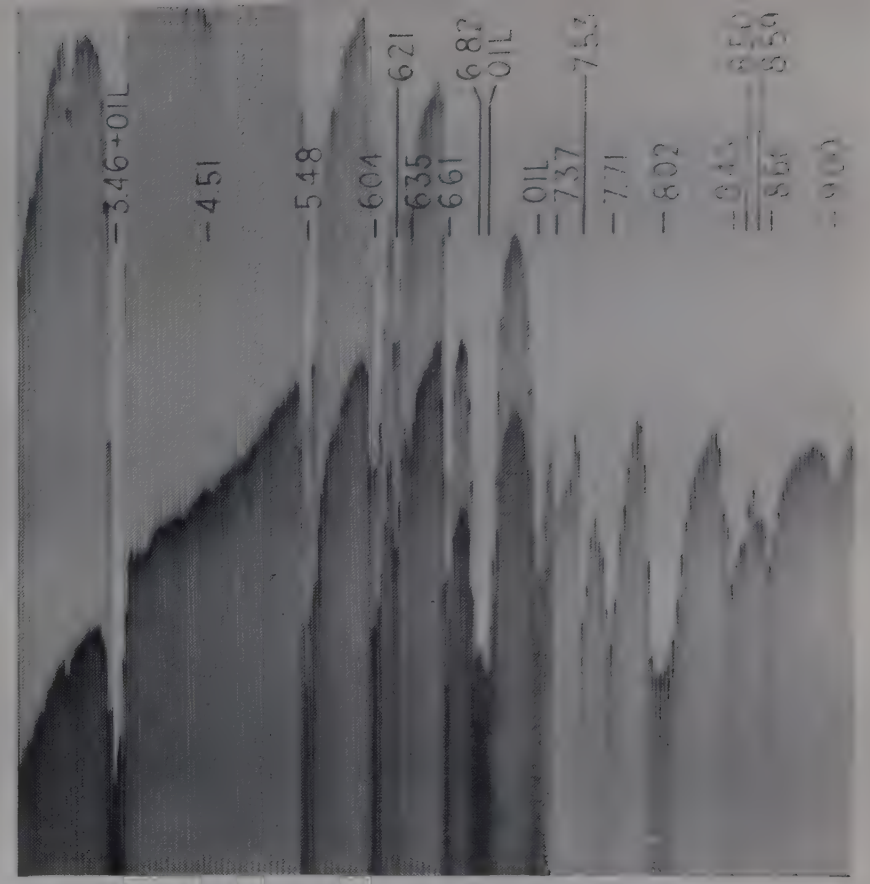


PLATE 166. Assignments: 5.48 μ C=O
6.04 μ C=N
6.21 μ, 6.35 μ, 6.61 μ } Conjugated phenyl
Preparations: Oil paste

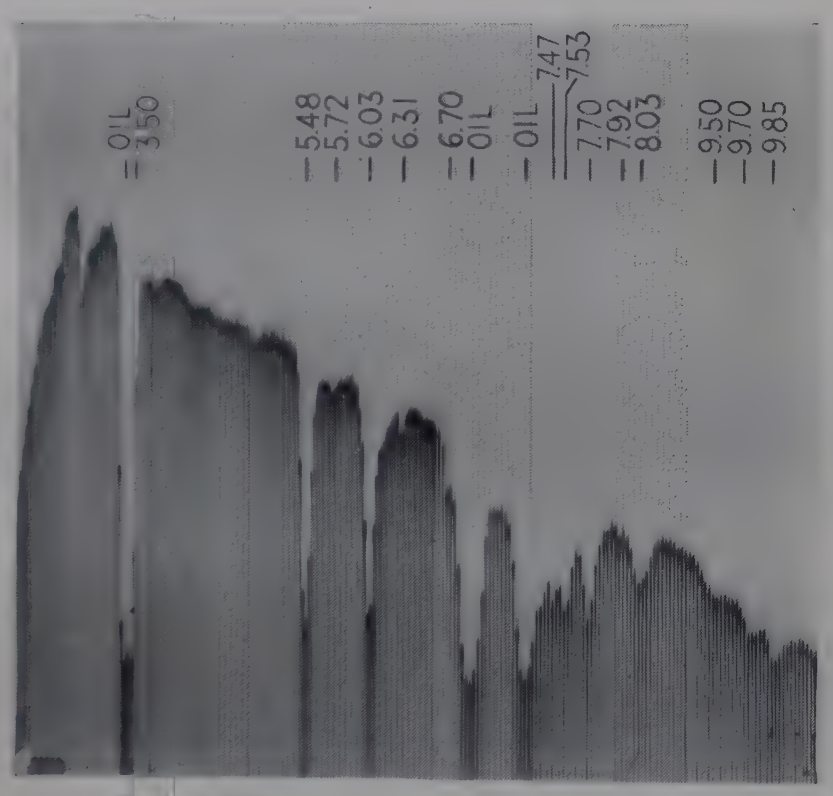


PLATE 167. Assignments: 5.48 μ C=O
6.03 μ C=N
Preparations: Oil paste

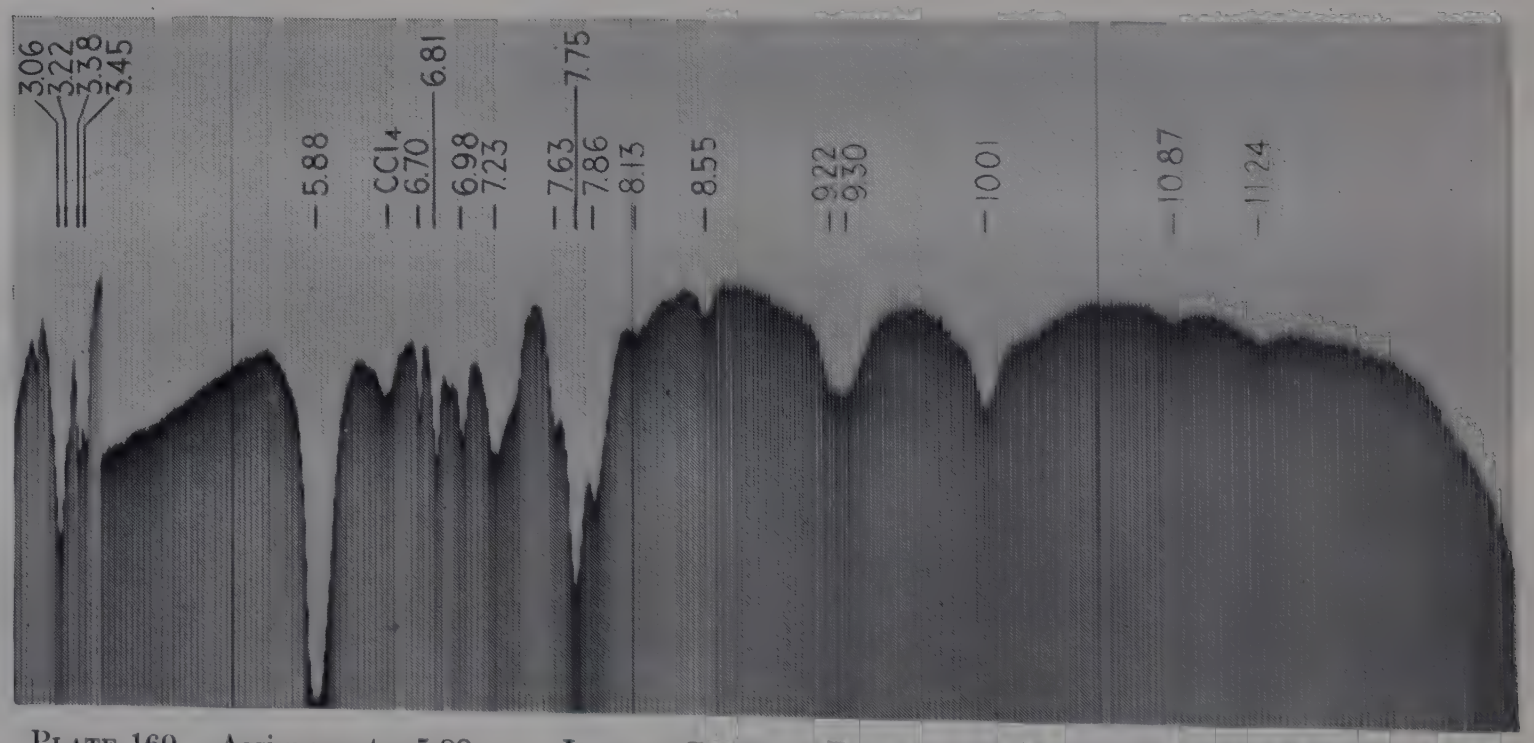


PLATE 169. Assignments: 5.88 μ Lactam C=O Preparations: 10% solution in CCl_4, 0.04 mm.

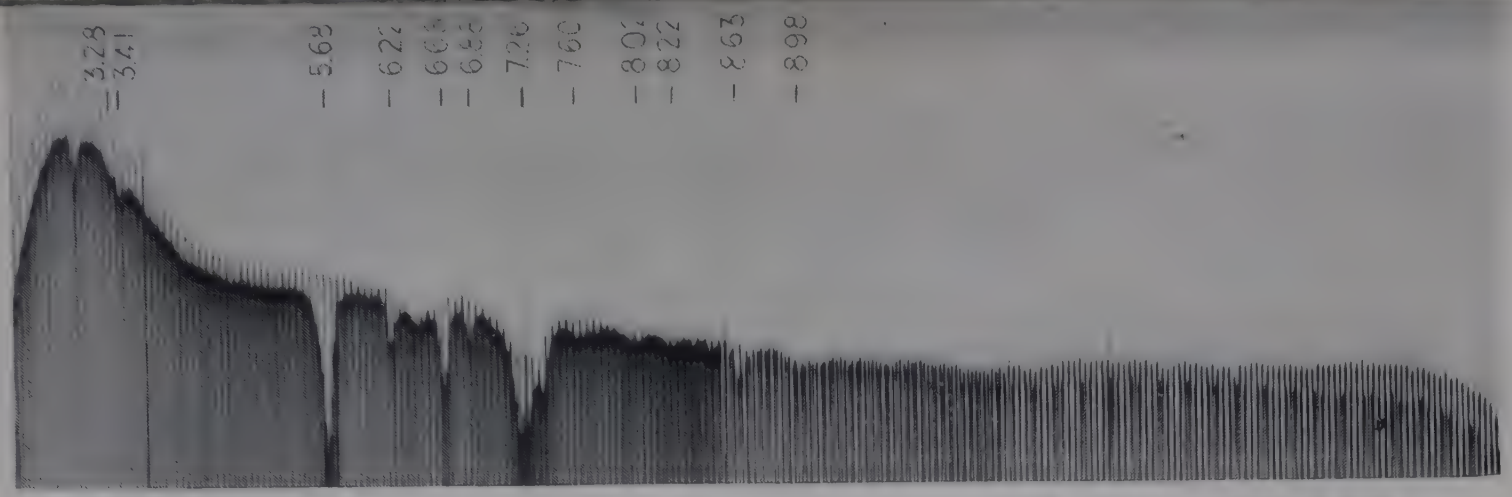
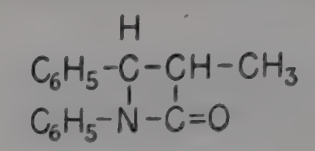
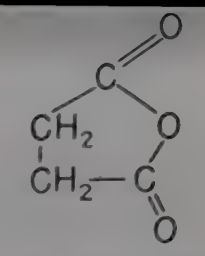


PLATE 170. Assignments: 5.68 μ Lactam C=O Preparations: 3% solution in CCl_4, 0.015 mm.

PROPIONIC LACTAM

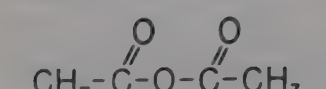


(*Top*)



(*Bottom Left*)

ACETIC ANHYDRIDE



(*Middle*)

KETENE

$H_2C=C=O$

(*Bottom Right*)

PLATE 172. Preparations: 0.015 mm.

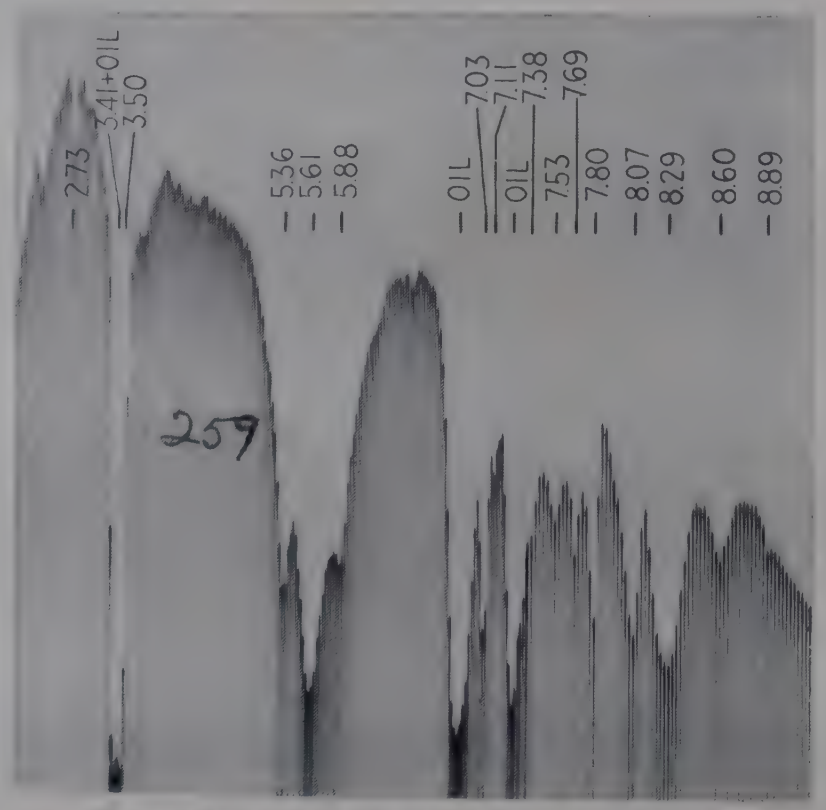
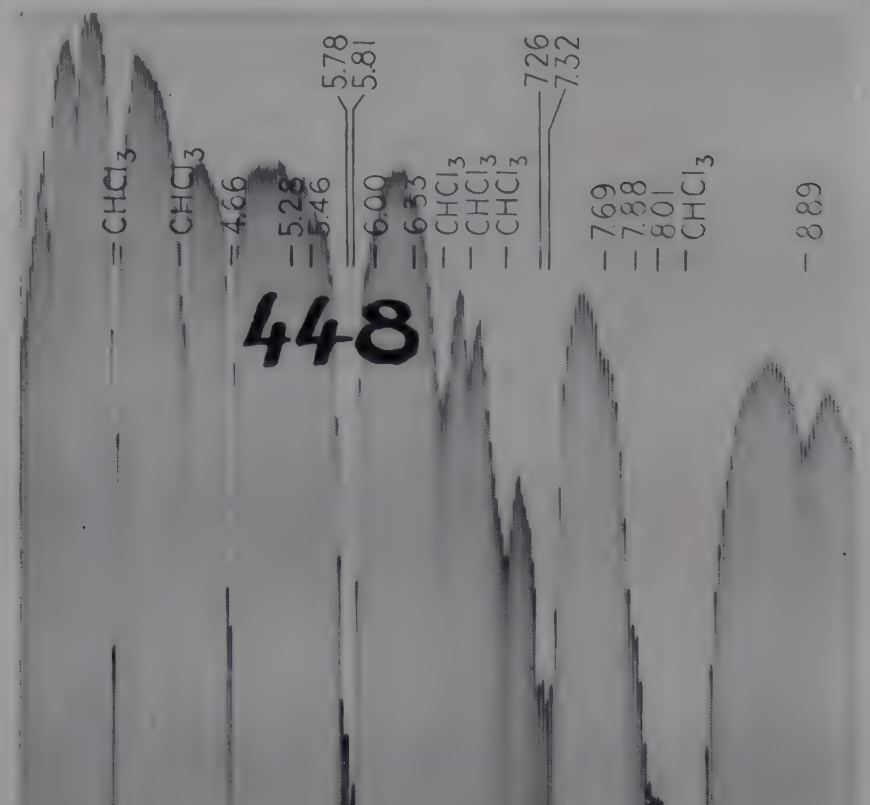


PLATE 171. 5.36 μ, 5.61 μ Anhydride C=O;



KETENE DIMER

$(H_2C=C=O)_2$

(Both plates)

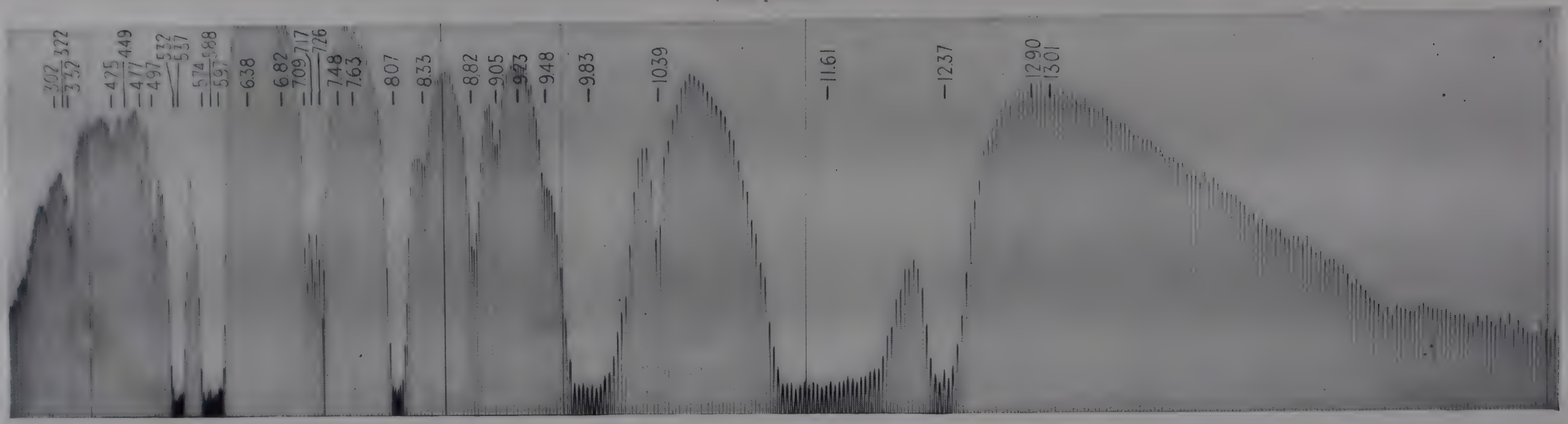


PLATE 174. Preparations: 0.015 mm.

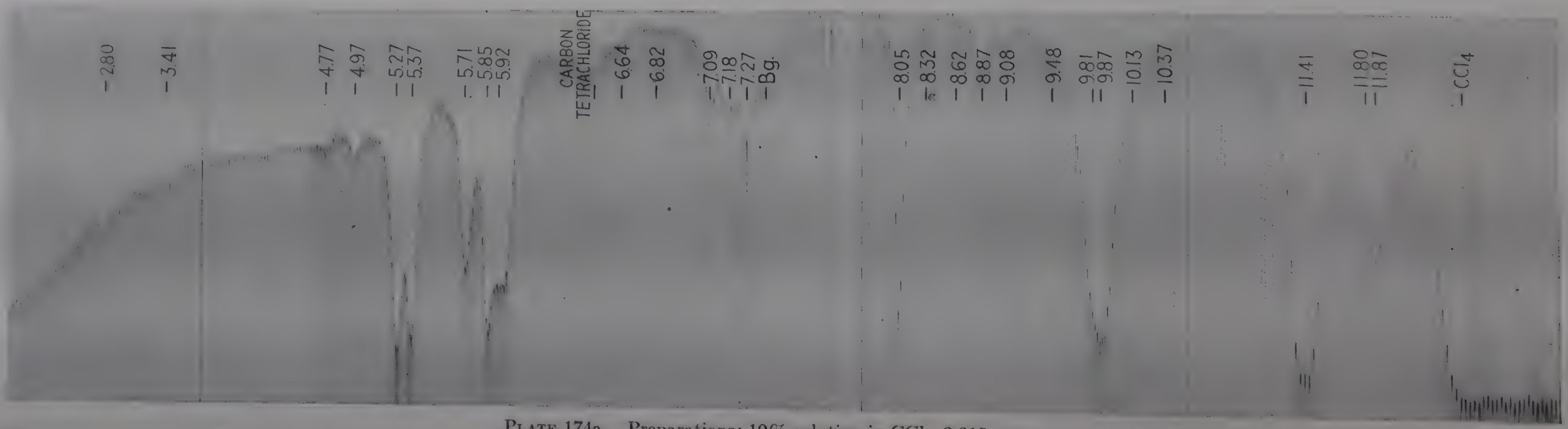


PLATE 174a. Preparations: 10% solution in CCl_4, 0.015 mm.

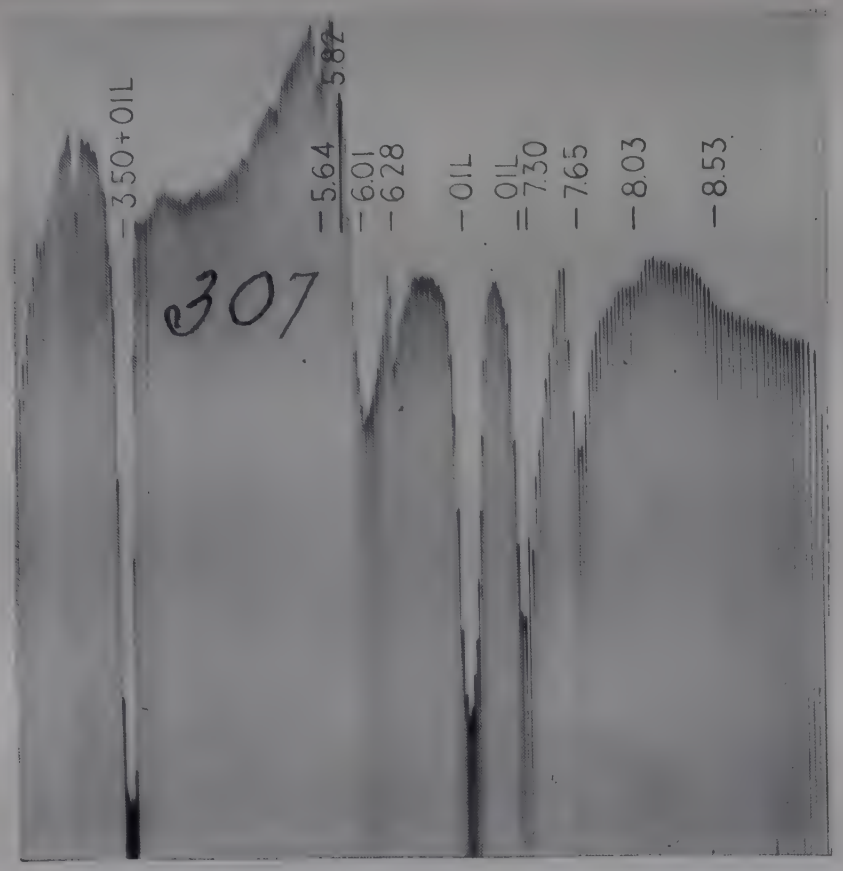
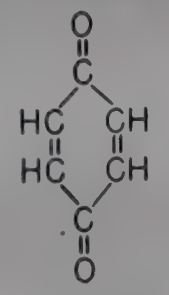


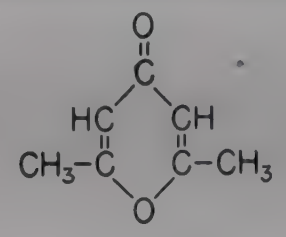
PLATE 176. Assignments: 6.01 μ Keto C=O
6.28 μ C=C conjugated
Preparations: Oil paste

QUINONE



(Top Left)

2,6 DIMETHYLPYRONE



(Top Right)

DIPHENYLKETENE

$(C_6H_5)_2$ C=C=O

(Bottom)

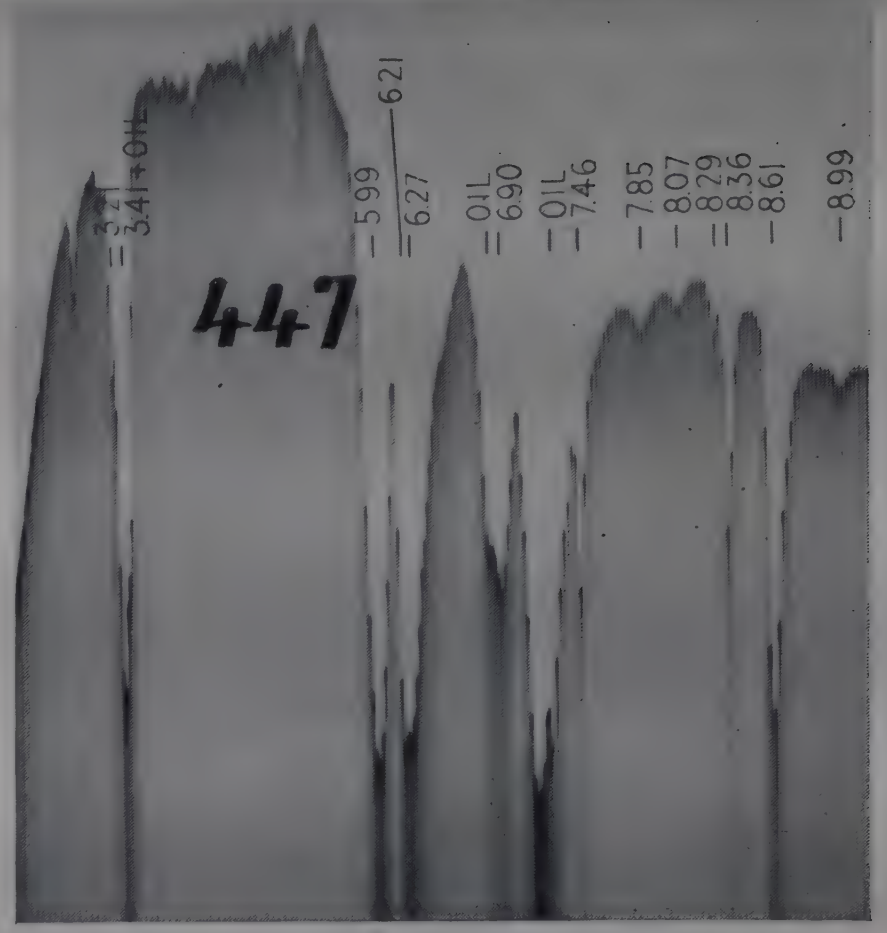


PLATE 179. Assignments: 5.99 μ Keto C=O
6.21 μ, 6.27 μ Ring vibrations
Preparations: Oil paste

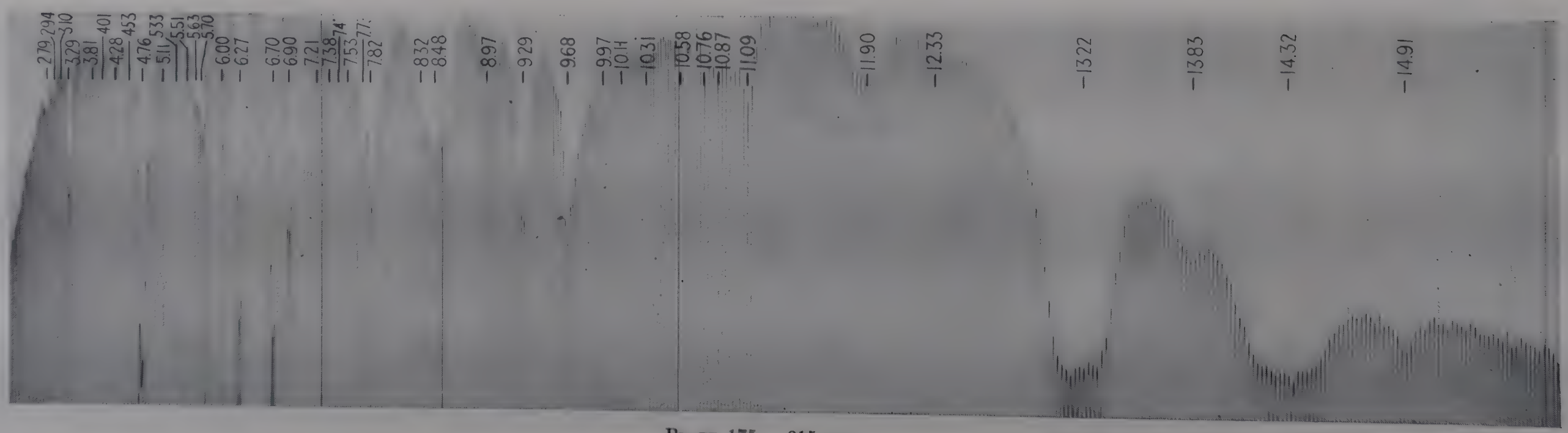


PLATE 175. .015 mm.

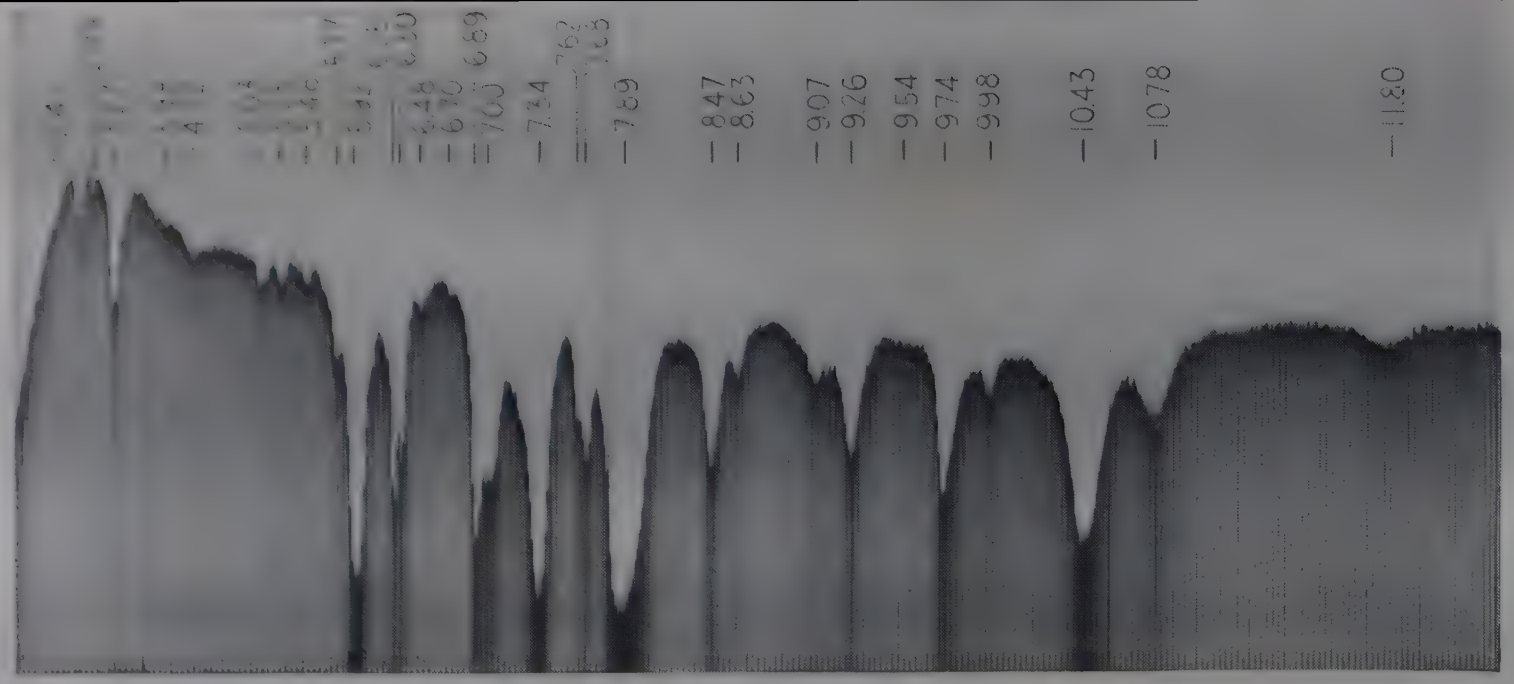
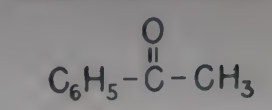


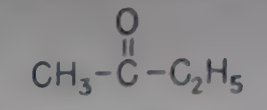
PLATE 180. Assignments: 5.92 μ Keto C=O conjugated Preparations: 0.015 mm.

ACETOPHENONE



(*Top*)

METHYL ETHYL KETONE



(*Bottom Left*)

PYRUVIC ACID METHYL ESTER

(*Bottom Right*)

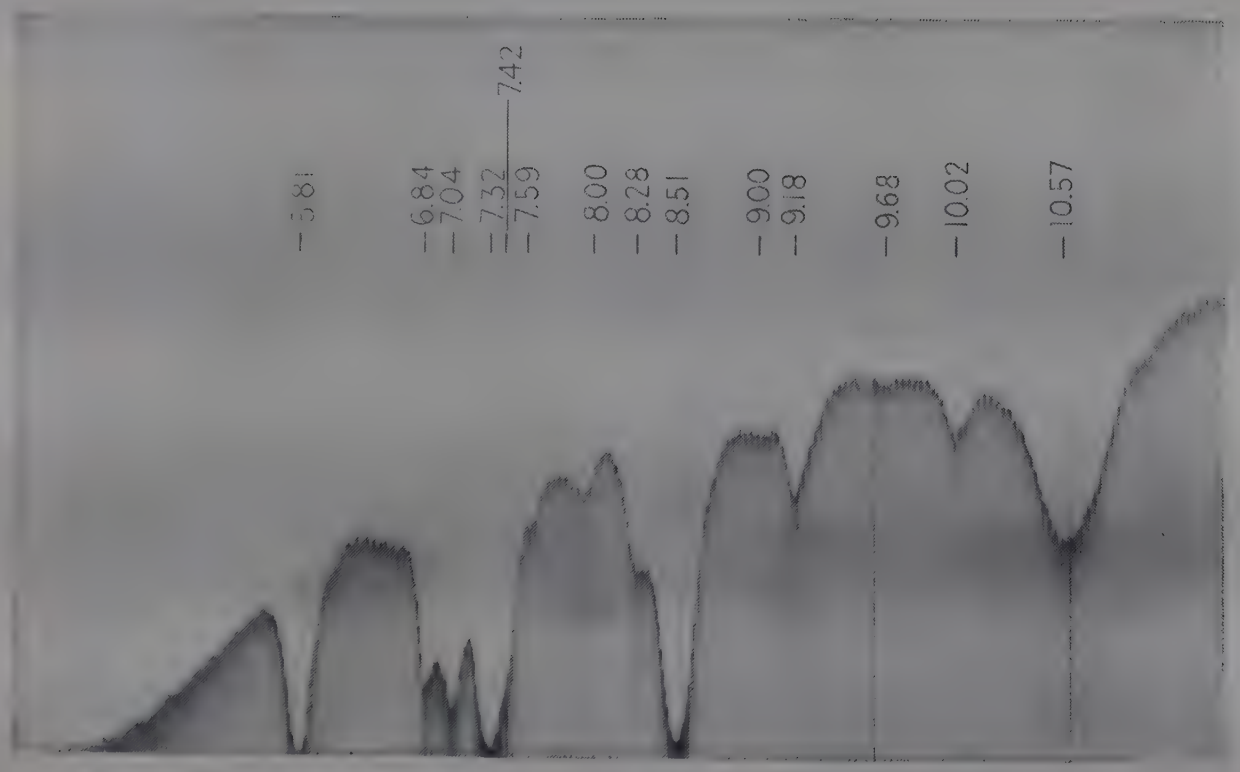


PLATE 177. Assignments: 5.81 μ Keto C=O Preparations: 0.015 mm.

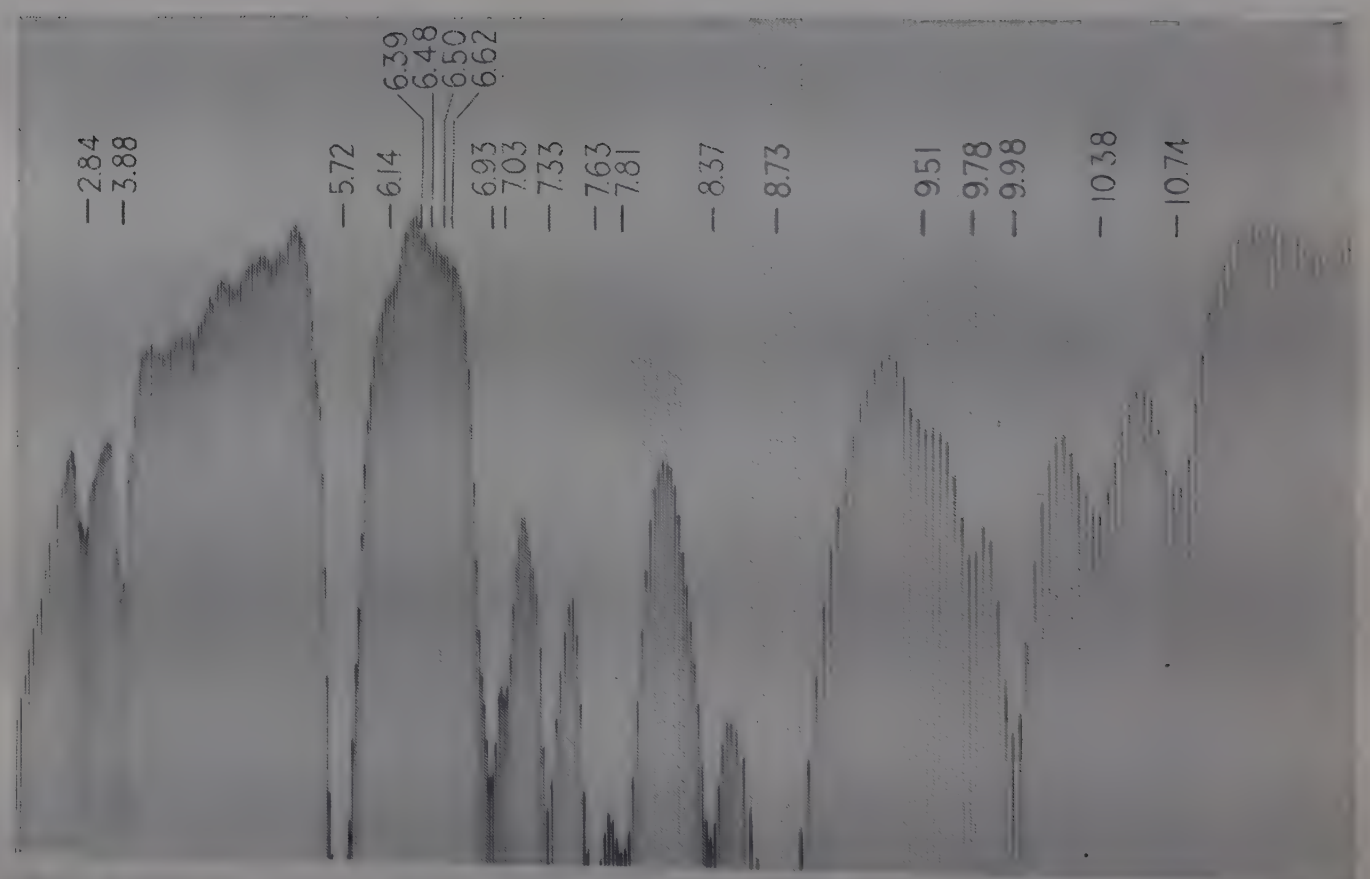


PLATE 178. Assignments: 5.72 μ Ester C=O, Keto C=O Preparations: 0.015 mm.

BIACETYL

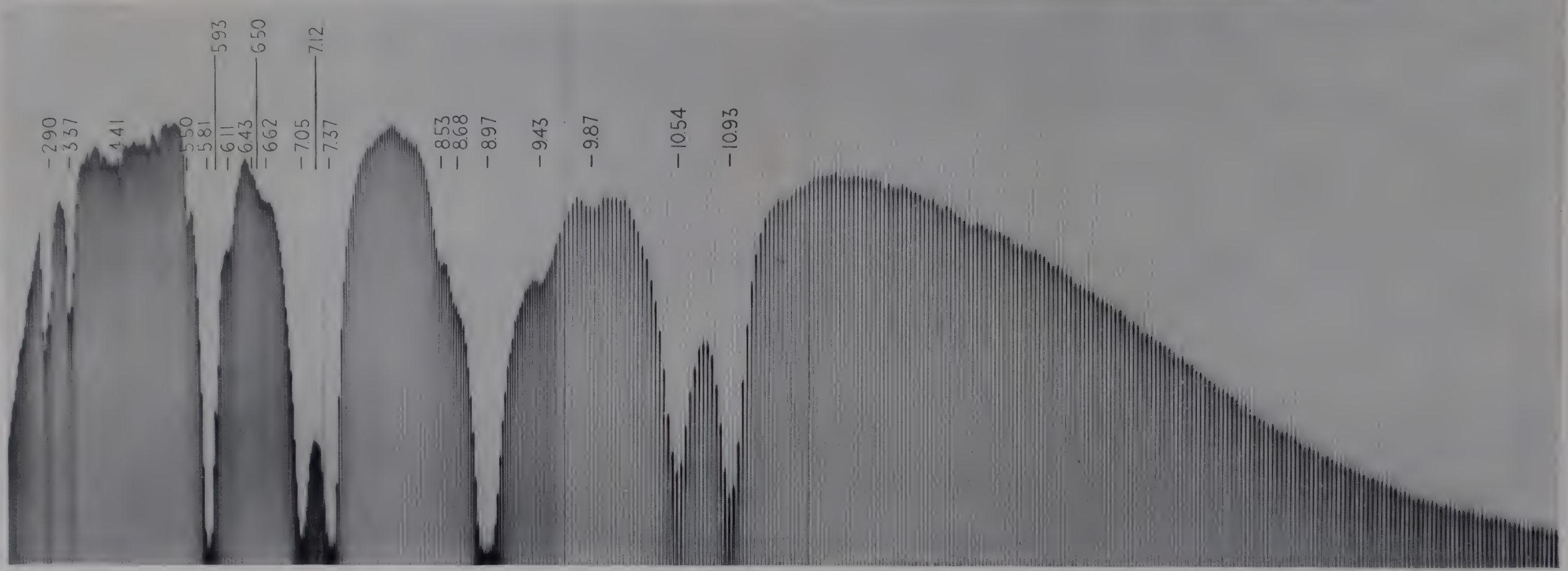
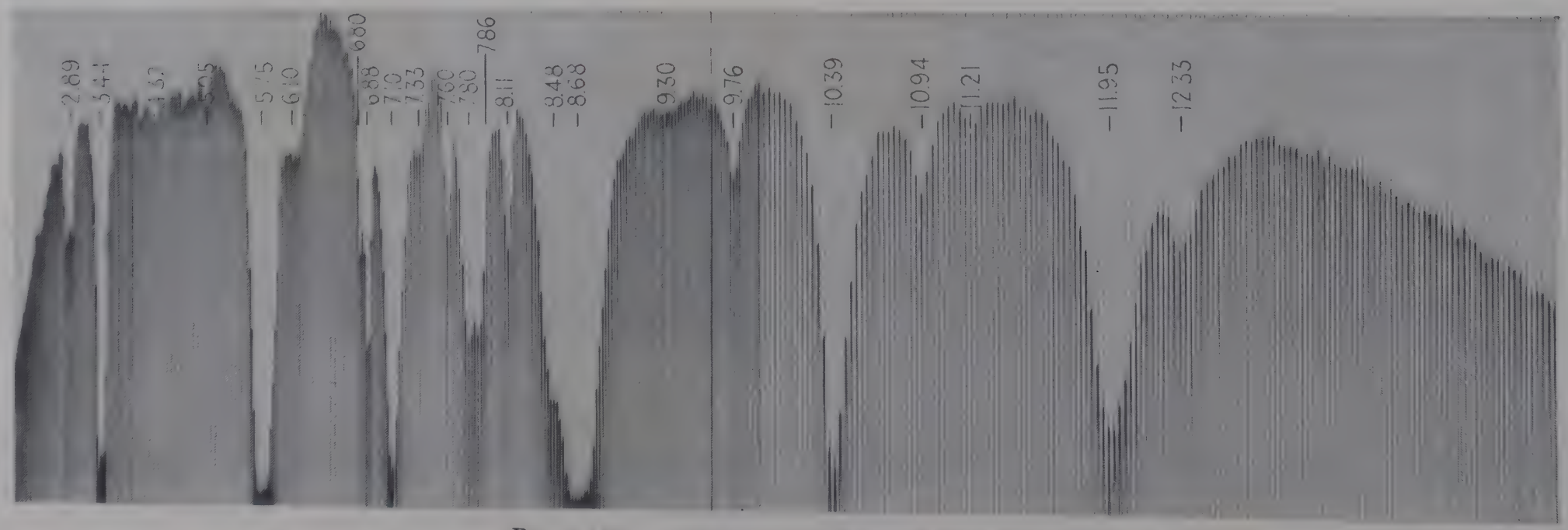


PLATE 181. Assignments: 5.81 μ Keto C=O Preparations: 0.02 mm.



CYCLOPENTANONE

PLATE 182. Assignments: 5.75 μ Keto C=O, cyclic Preparations: 0.02 mm.

BENZALDEHYDE

$C_6H_5-C(=O)H$

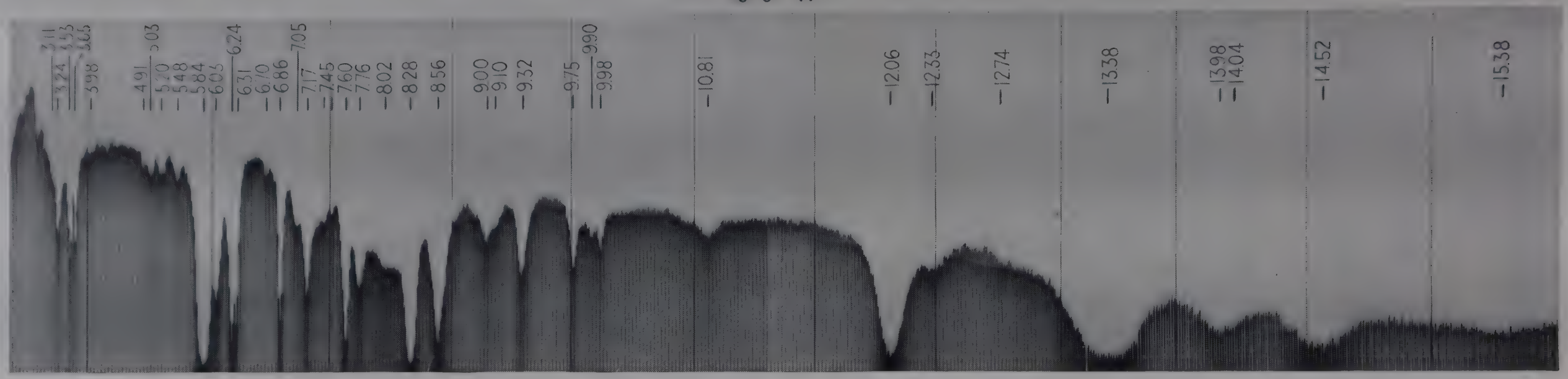


PLATE 184. Assignments: 5.84 μ Aldehyde C=O (conjugated) Preparations: 0.015 mm.

6.24 μ, 6.31 μ, 6.70 μ } Phenyl

PROPIONALDEHYDE

$C_2H_5-CH=O$

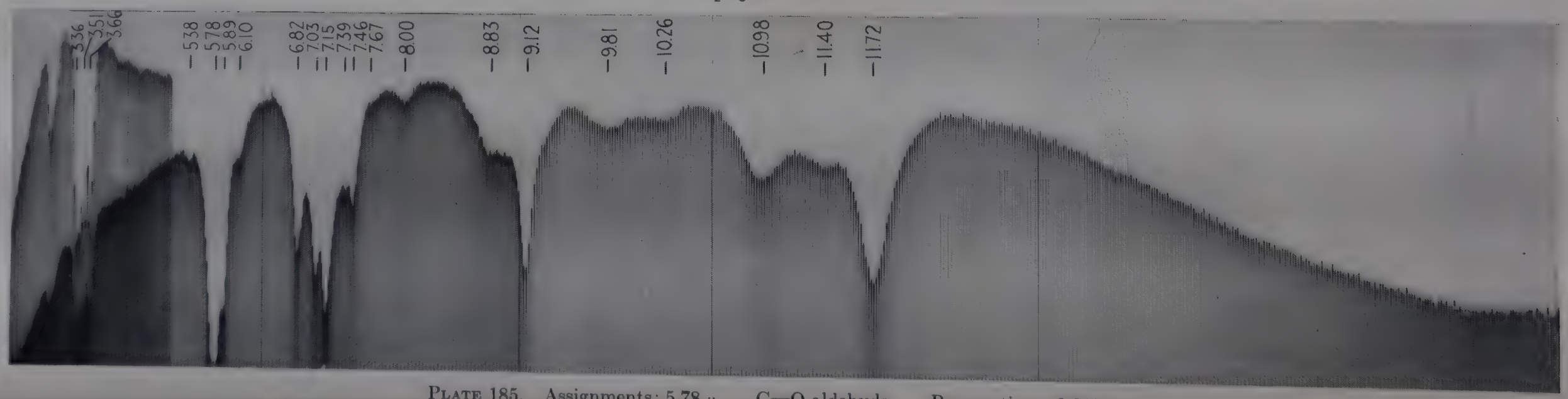


PLATE 185. Assignments: 5.78 μ C=O aldehyde Preparations: 0.015 mm.

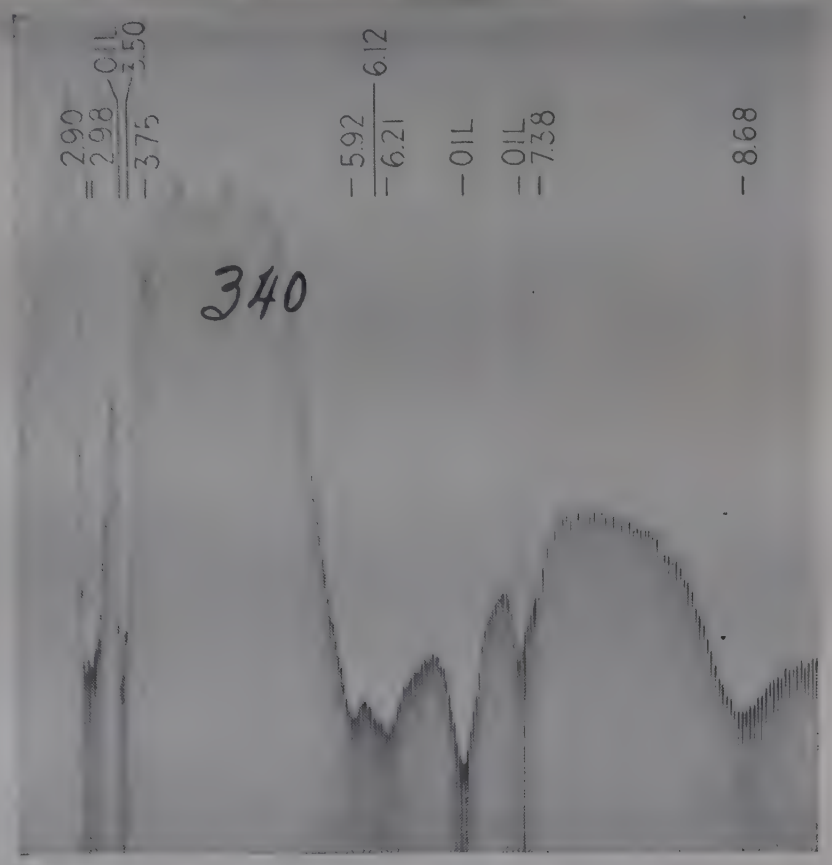
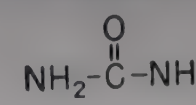


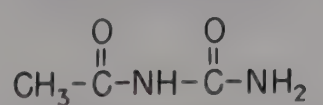
PLATE 186. Preparations: Oil paste

UREA



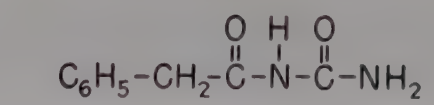
(Top Left)

ACETYLUREA



(Top Right)

PHENACETYLUREA



(Bottom)

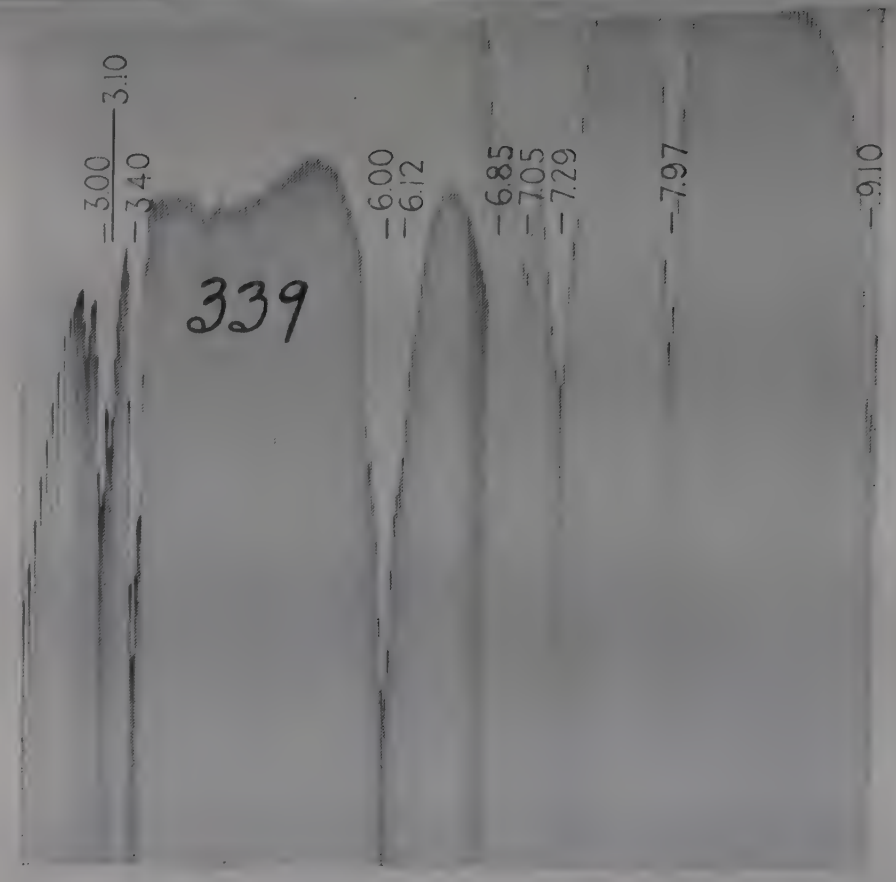


PLATE 188. Assignments: 6.00 μ N-acyl C=O
6.12 μ δNH_2
Preparations: Oil paste

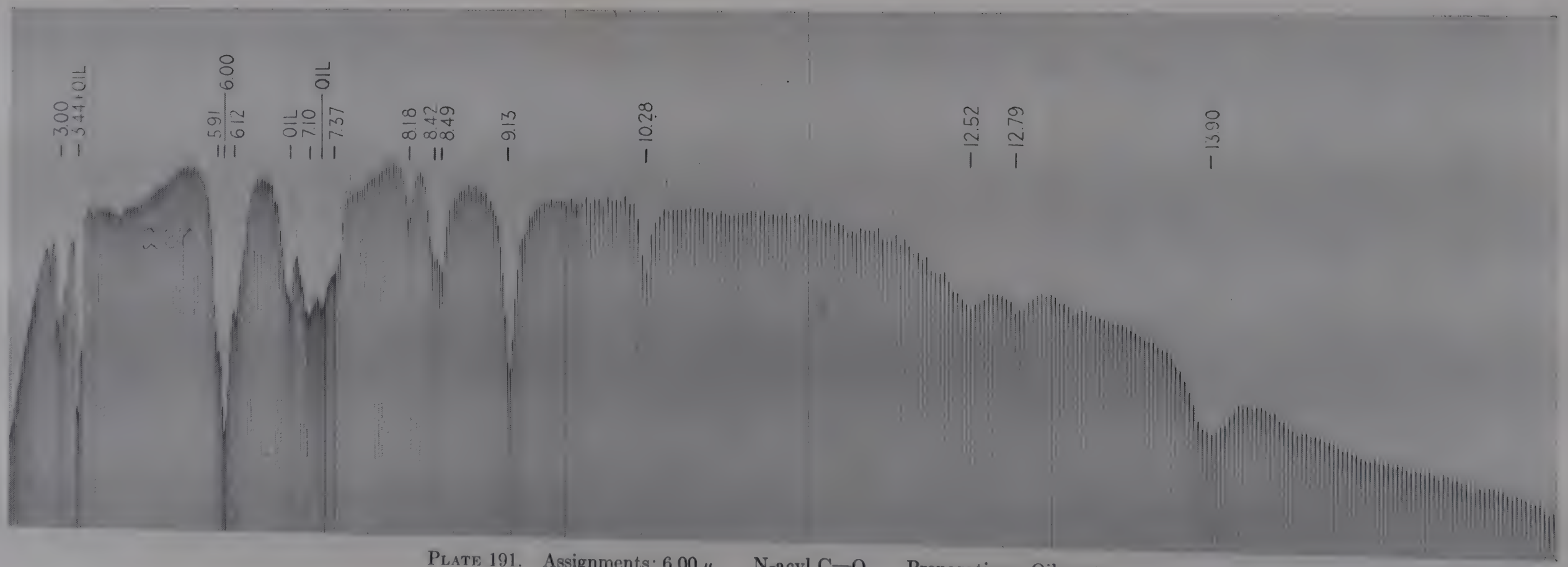


PLATE 191. Assignments: 6.00 μ N-acyl C=O
6.12 μ δNH_2
Preparations: Oil paste

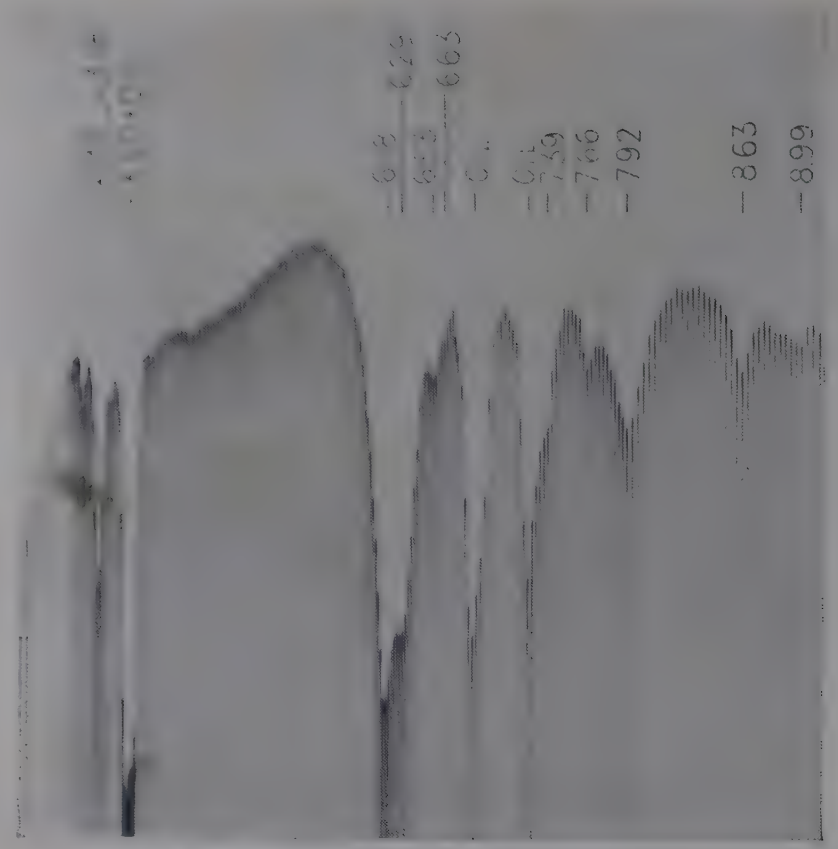


PLATE 187. Assignments: 6.18 μ Amide I
6.29 μ Unassigned
Preparations: Oil paste

SYM-DIETHYLUREA

(Top Left and Right)

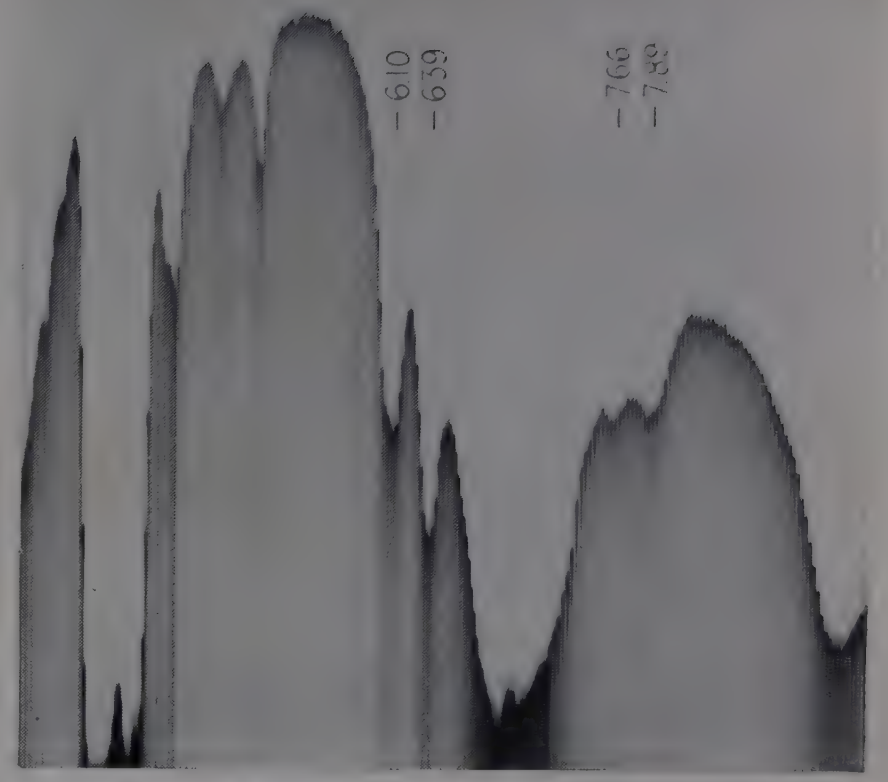


PLATE 187a. Preparations: Methanol solution, 0.02 mm.

PLATE 189. Assignments: 6.20 μ Unassigned
Preparations: Oil paste

THIOUREA

(Bottom Left)

ACETYLTHIOUREA

(Bottom Right)

PLATE 190. Assignments: 5.82 μ Unassigned
5.92 μ N-acyl C=O
6.25 μ δNH_2
6.48 μ Thioureide ion

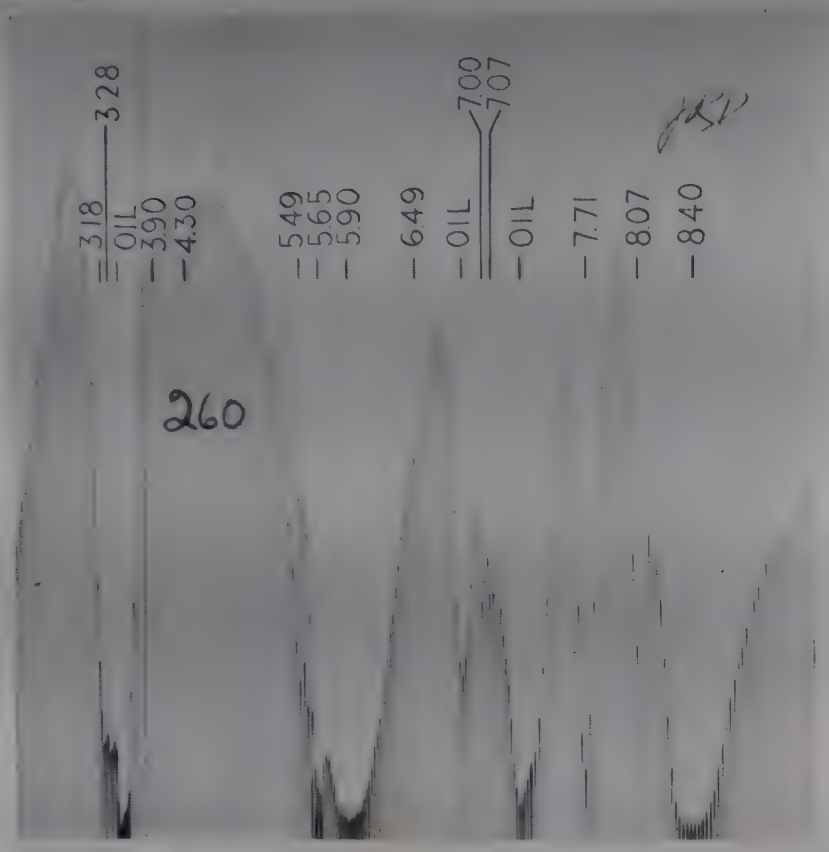
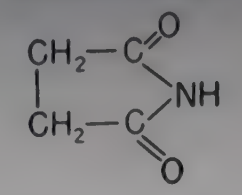


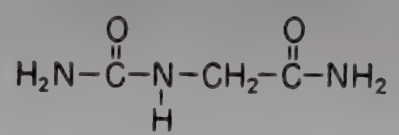
PLATE 192. Assignments: 5.65 μ 4-C=O
5.90 μ 2-C=O
Preparations: Oil paste

SUCCINIMIDE



(Top Left and Bottom)

HYDANTOIC AMIDE



(Top Right)

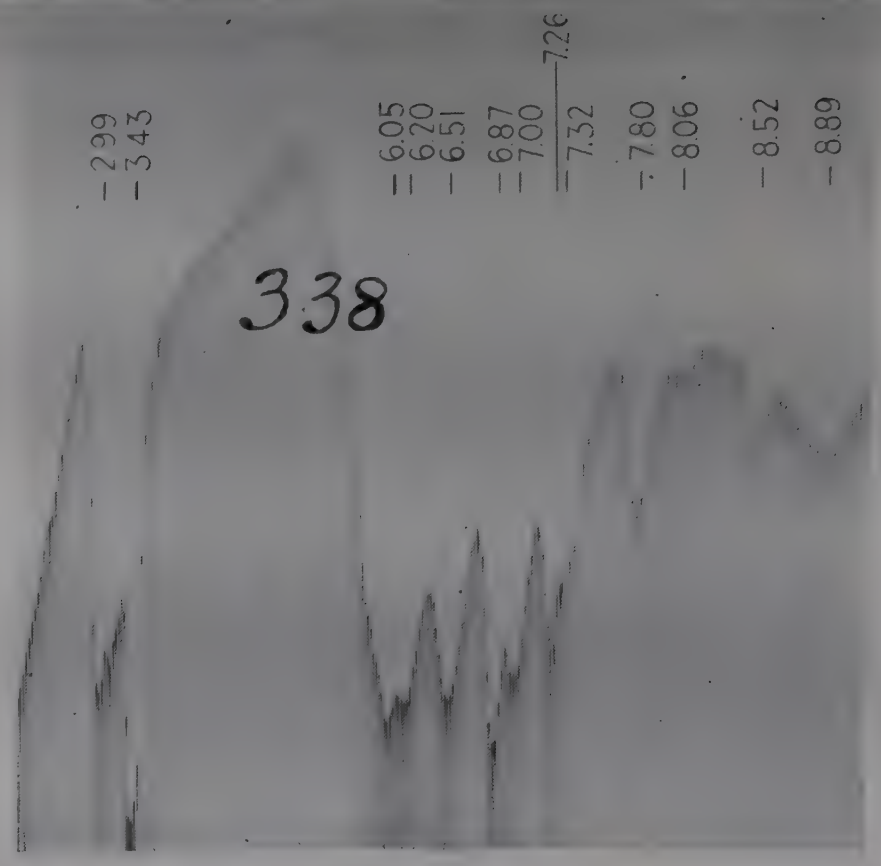


PLATE 193. Assignments:
6.05 μ NH_2 amide type C=O
6.20 μ Unassigned
6.51 μ Amide II
Preparations: Oil paste

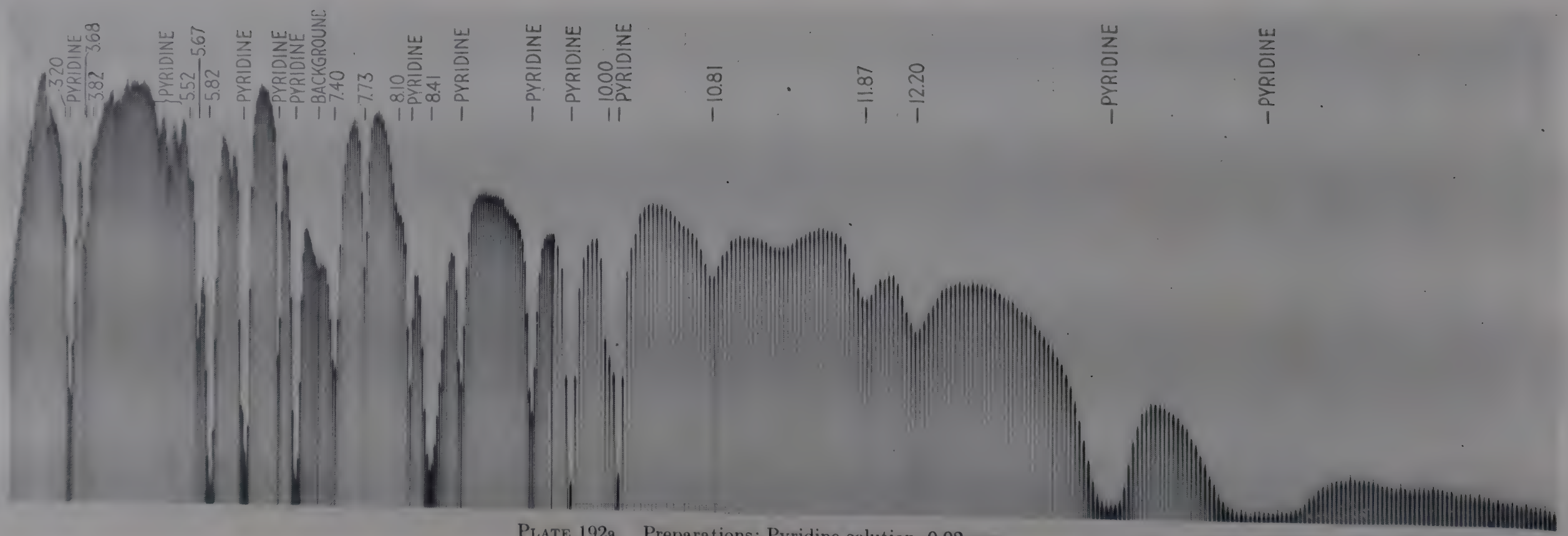
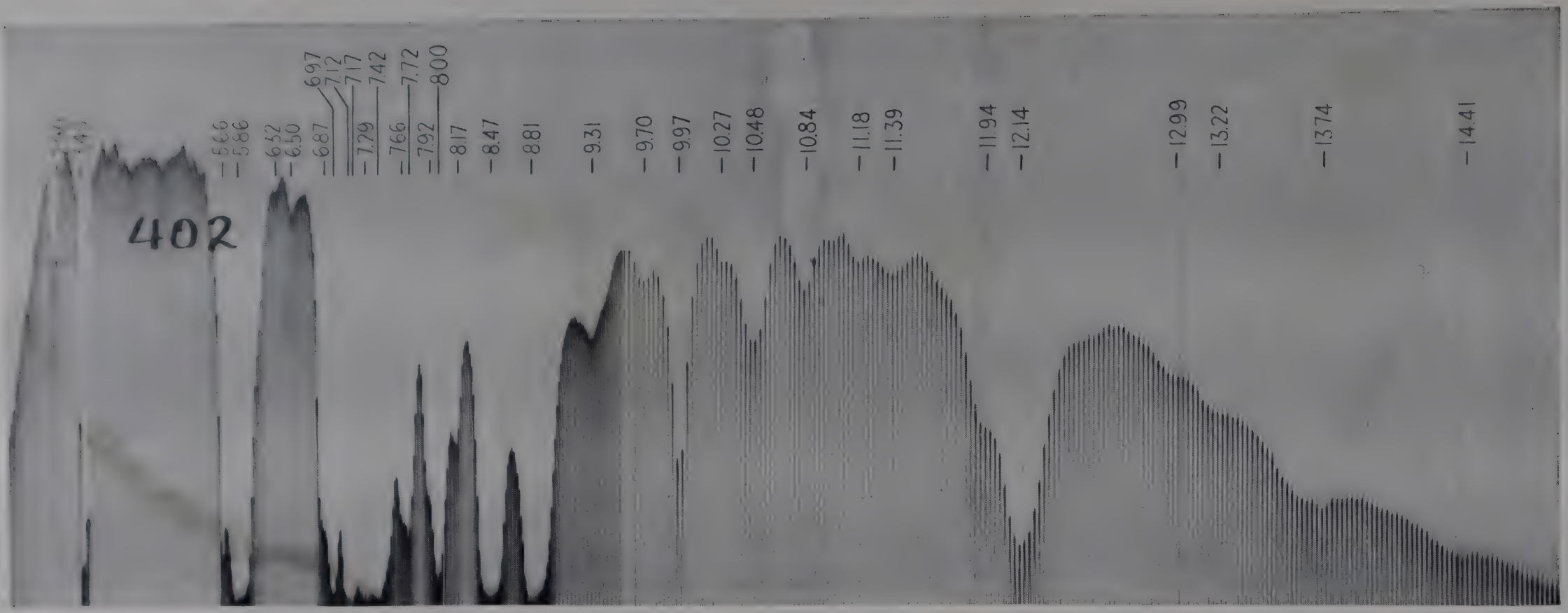


PLATE 192a. Preparations: Pyridine solution, 0.02 mm.



N-(n-AMYL)-SUCCINIMIDE

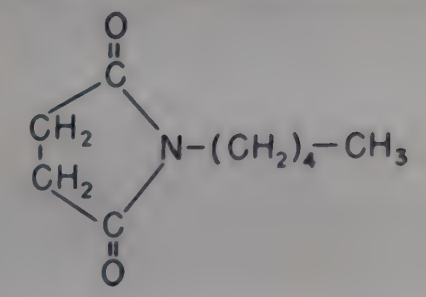
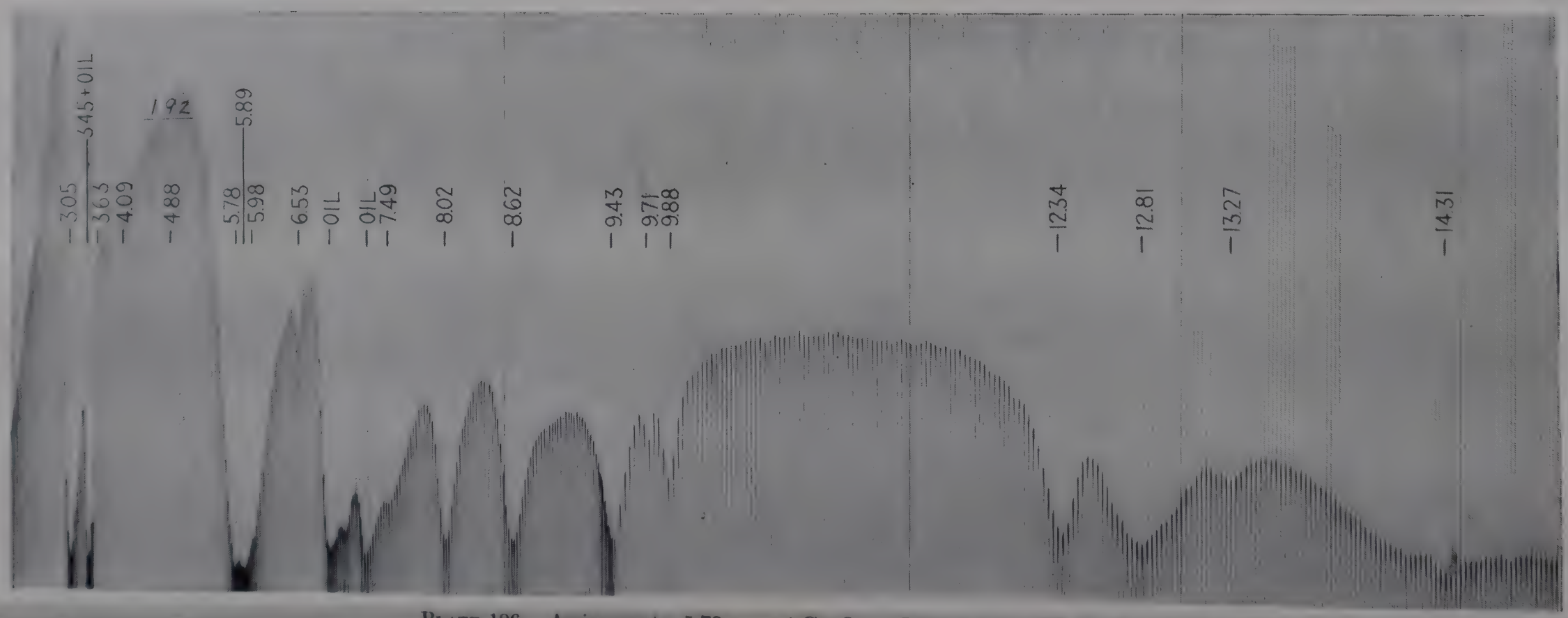


PLATE 195. Assignments: 5.66 μ 4-C=O 5.86 μ 2-C=O Preparations: 0.02 mm.



ALLOXAN MONOHYDRATE

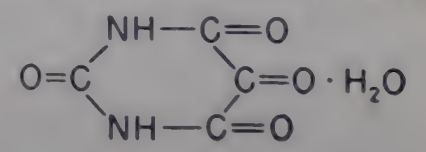
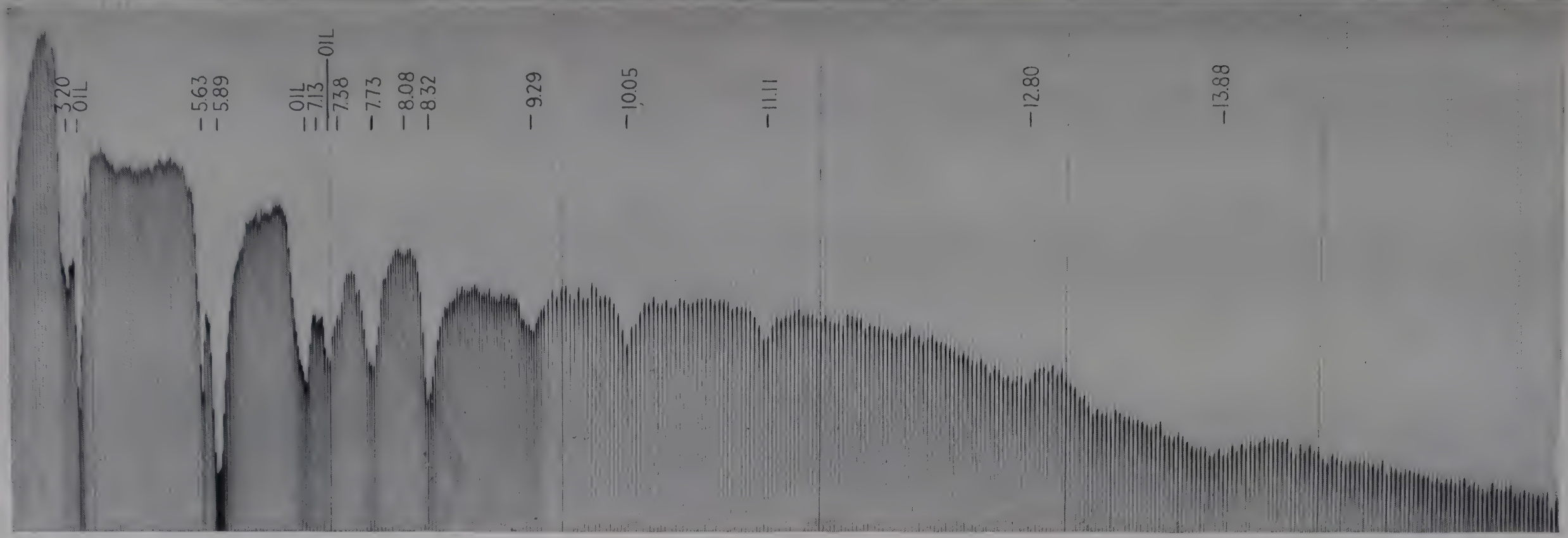


PLATE 196 Assignments: 5.78 μ 4-C=O Preparations: Oil paste



HYDANTOIN

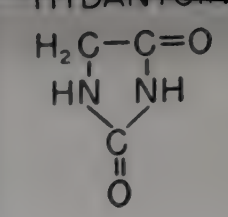
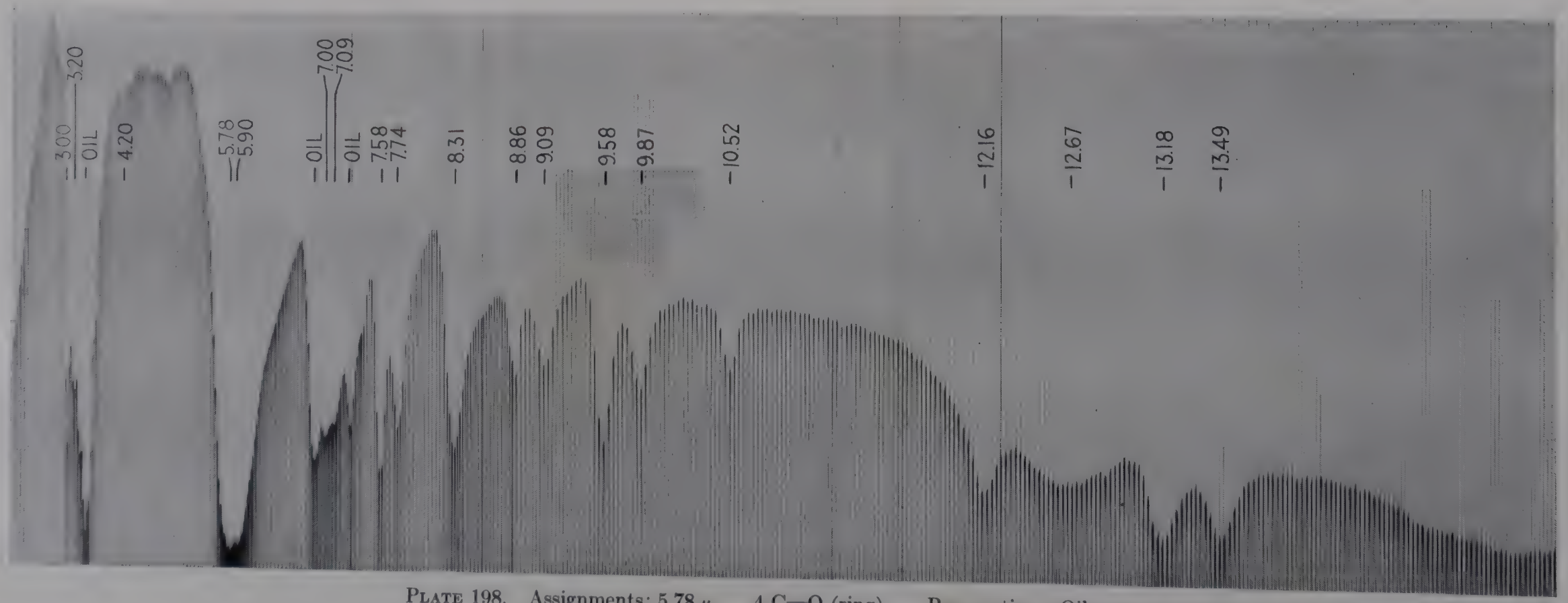


PLATE 197. Assignments: 5.63 μ 4-C=O (ring) Preparations: Oil paste
5.89 μ 2-C=O (ring)



5-METHYLHYDANTOIN

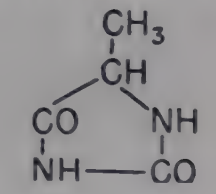


PLATE 198. Assignments: 5.78 μ 4-C=O (ring) Preparations: Oil paste
5.90 μ 2-C=O (ring)

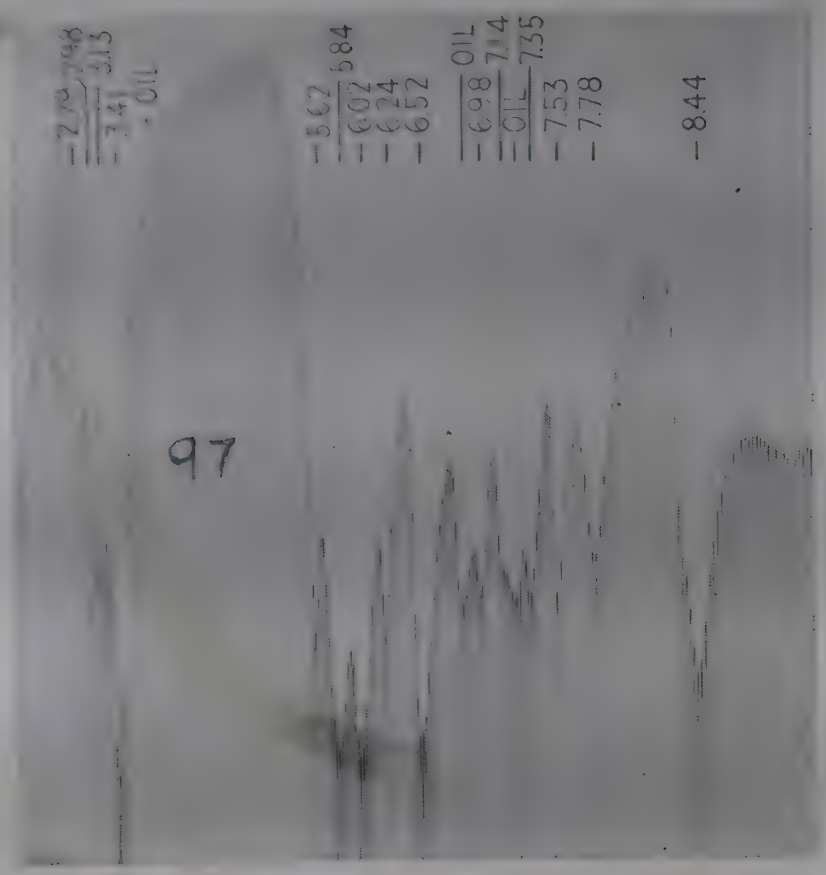
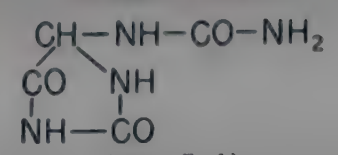


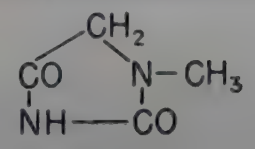
PLATE 194. Assignments: 5.62 μ 4-C=O (ring)
5.84 μ 2-C=O (ring)
6.02 μ Amide I
6.52 μ Amide II
Preparations: Oil paste

ALLANTOIN



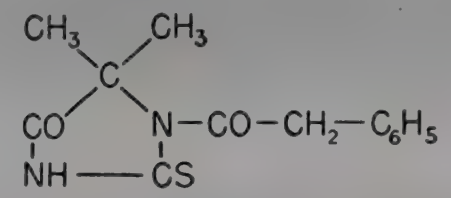
(Top Left)

1-METHYLHYDANTOIN



(Top Right)

1-PHENACETYL-5,5-DIMETHYL-2-THIOHYDANTOIN



(Bottom)

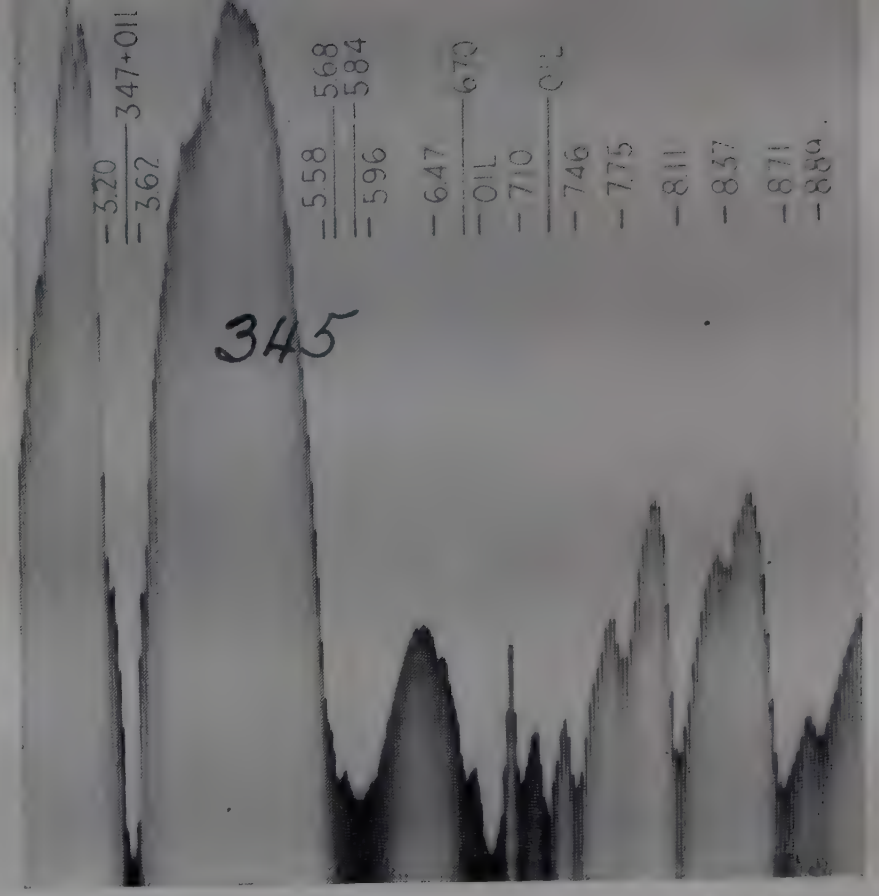


PLATE 199. Assignments: 5.68 μ 4-C=O
5.84 μ 2-C=O
Preparations: Oil paste

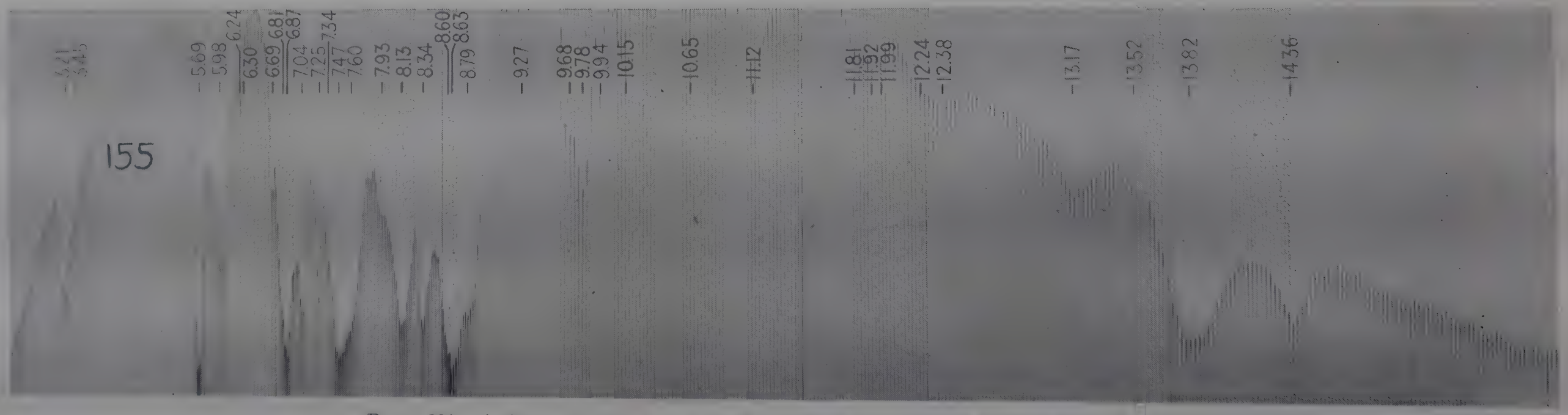


PLATE 201. Assignments: 5.69 μ 4-C=O (ring)
5.98 μ Acyl C=O
6.81 μ Thioureide ion
Preparation: Deposited from pyridine

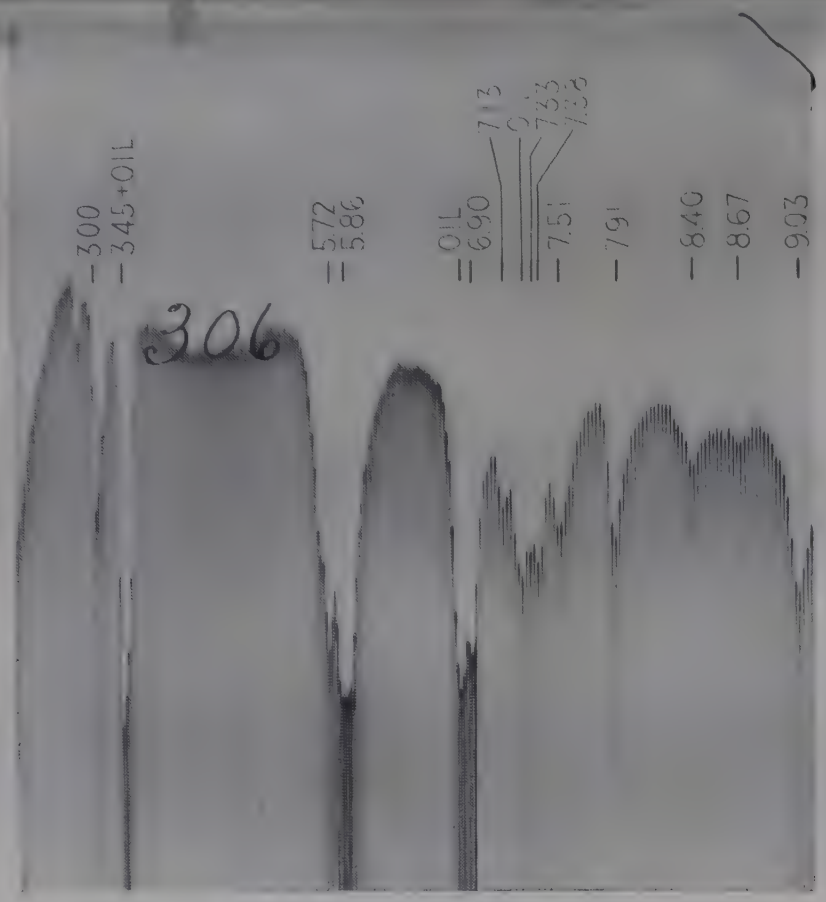
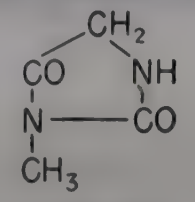


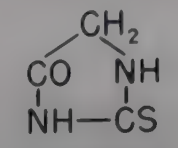
PLATE 200. Assignments: 5.72 μ 4-C=O
5.86 μ 2-C=O
Preparations: Oil paste

3-METHYLHYDANTOIN



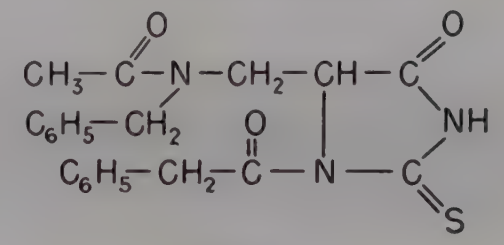
(Top Left)

2-THIOHYDANTOIN



(Top Right)

1-PHENACETYL-5-(N-BENZYLACETAMIDOMETHYL)-2-THIOHYDANTOIN



(Bottom)

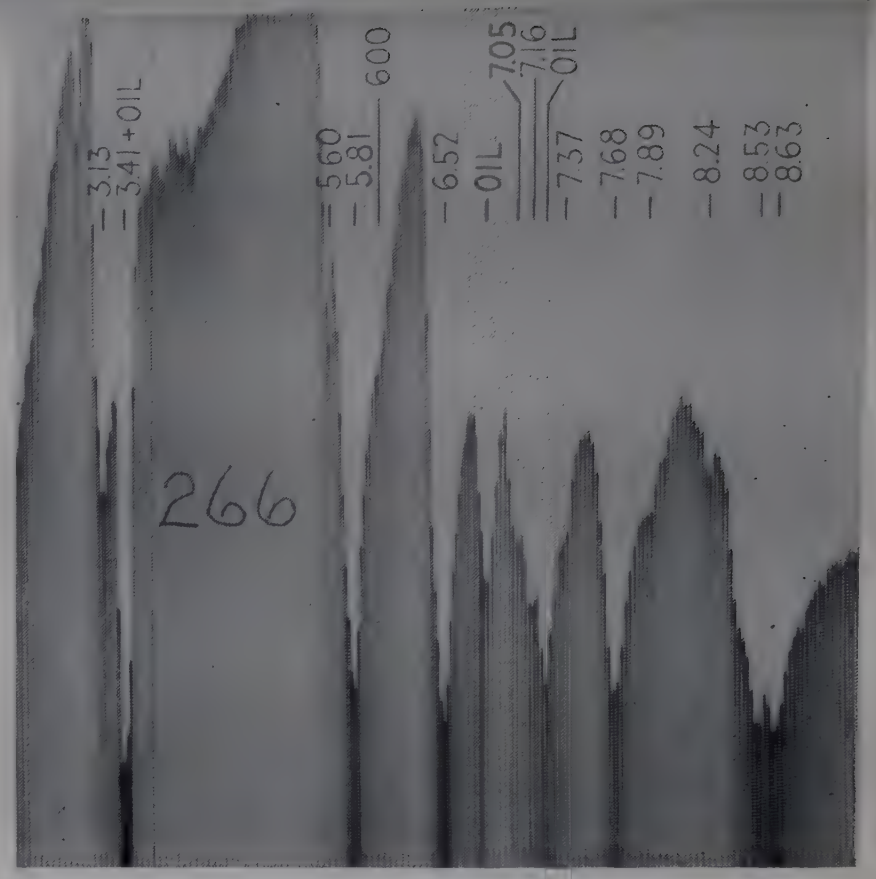


PLATE 204. Assignments: 5.81 μ 4-C=O
6.52 μ Thioureide ion
Preparation: Oil paste

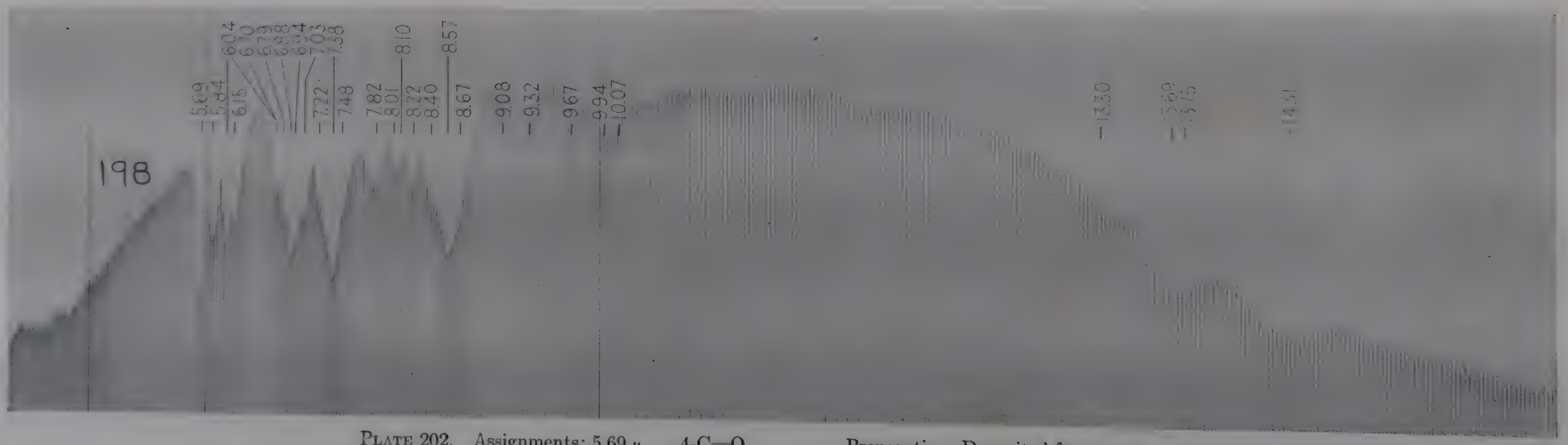
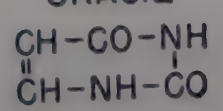


PLATE 202. Assignments: 5.69 μ 4-C=O
5.84 μ 1-acyl
6.04 μ N-acyl C=O
6.79 μ Thioureide ion
Preparation: Deposited from acetone

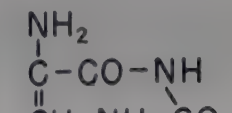
PLATE 210. Assignments: 5.82 μ 4-C=O
6.01 μ 2-C=O
Preparation: Oil paste

URACIL



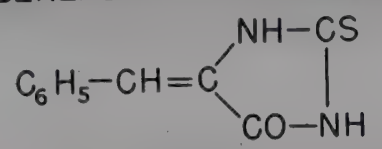
(Top Left)

5-AMINOURACIL



(Top Right)

5-BENZAL-2-THIOHYDANTOIN



(Bottom)

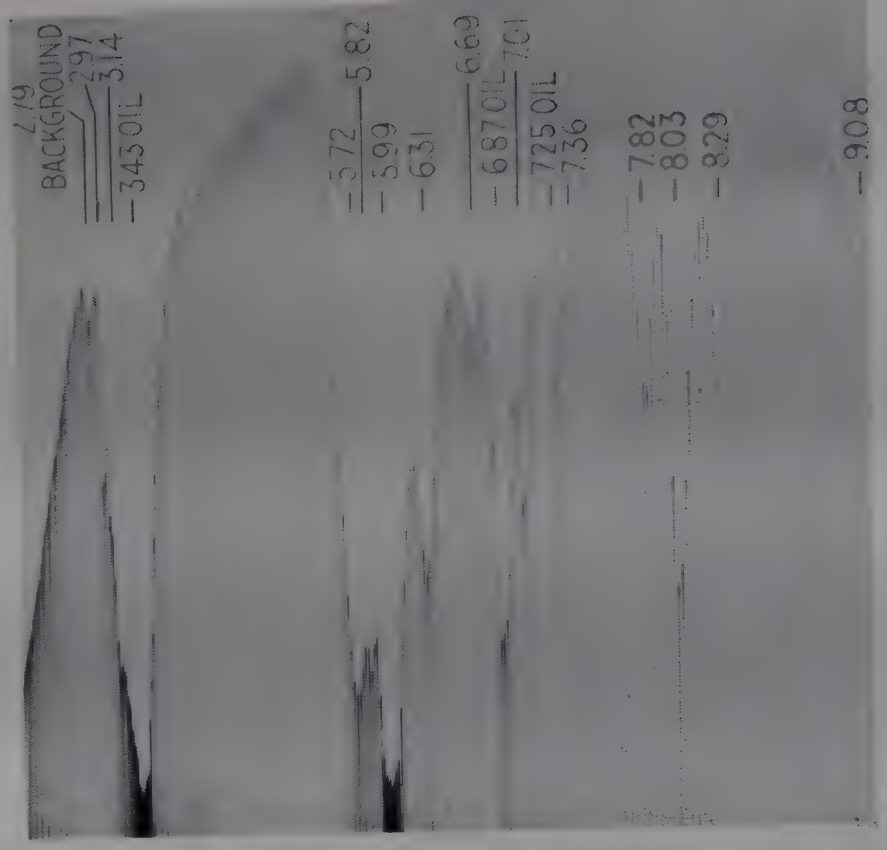


PLATE 211. Preparation: Oil paste

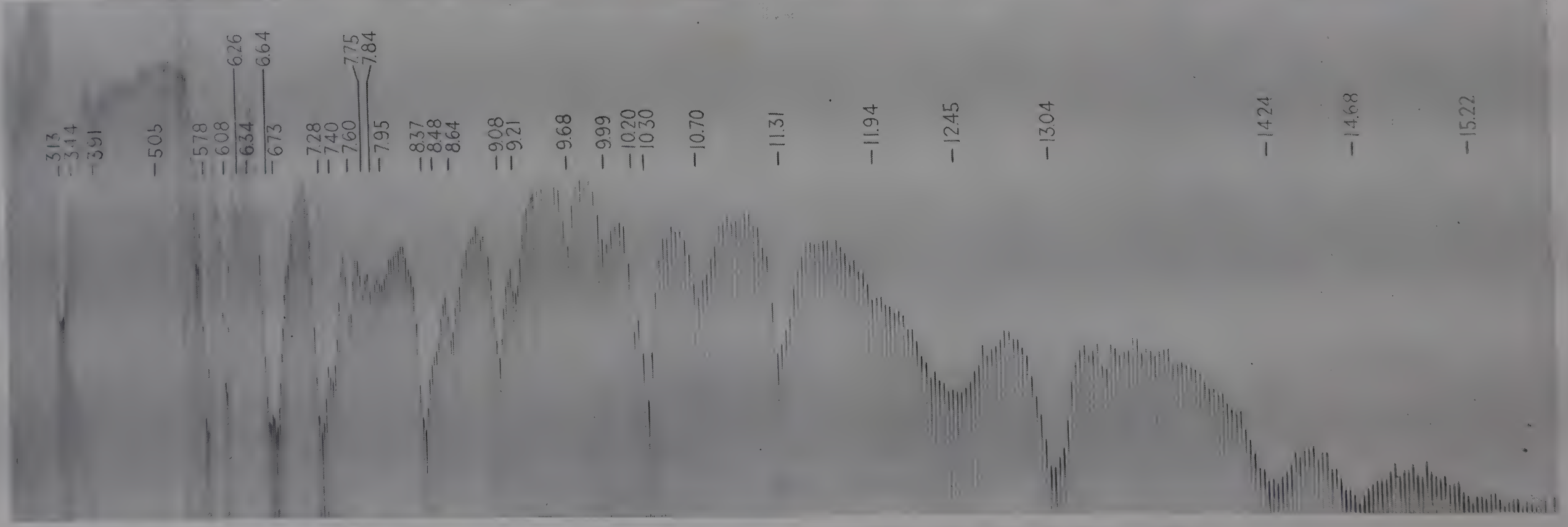


PLATE 203. Assignments: 5.78 μ 4-C=O
6.08 μ C=C
6.26 μ, 6.34 μ, 6.64 μ Conjugated phenyl
Preparation: Deposited from pyridine

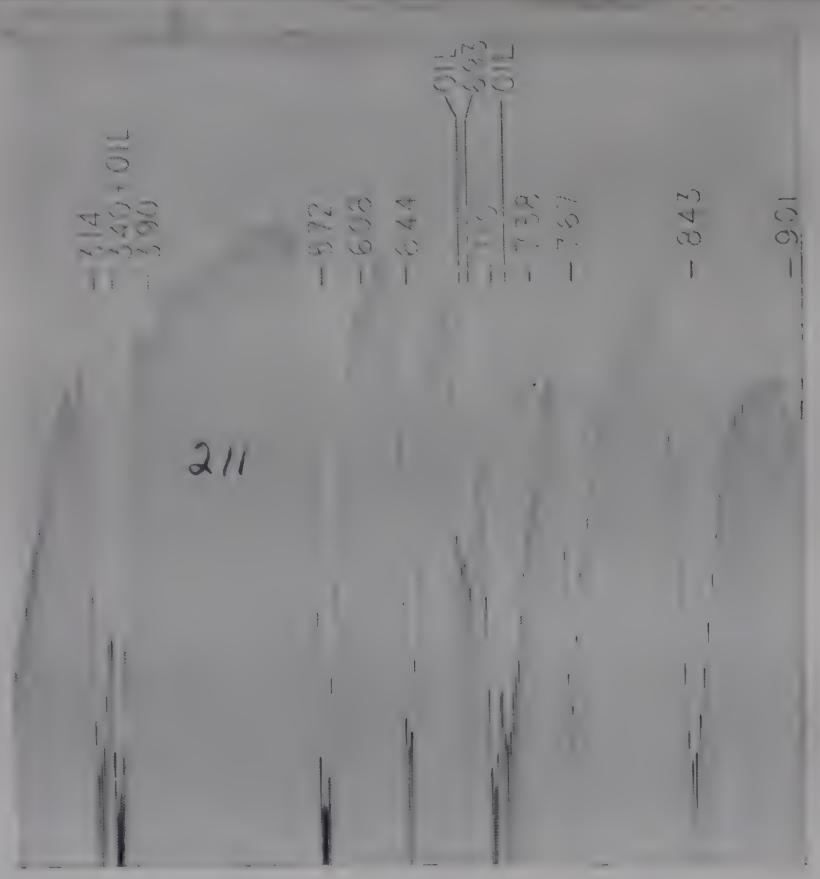
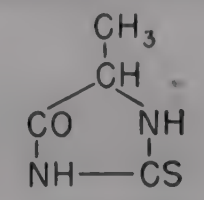


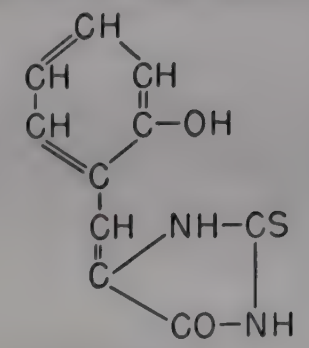
PLATE 205. Assignments: 5.72 μ 4-C=O
6.44 μ Thioureide ion
Preparation: Oil paste

5-METHYL-2-THIOHYDANTOIN



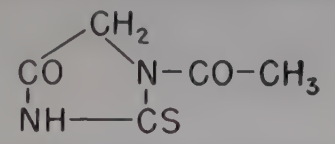
(Top Left)

2-THIOHYDANTOIN



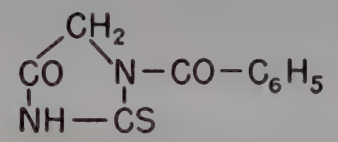
(Top Right)

1-ACETYL-2-THIOHYDANTOIN



Bottom Left and Center

1-BENZOYL-2-THIOHYDANTOIN



(Bottom Right)

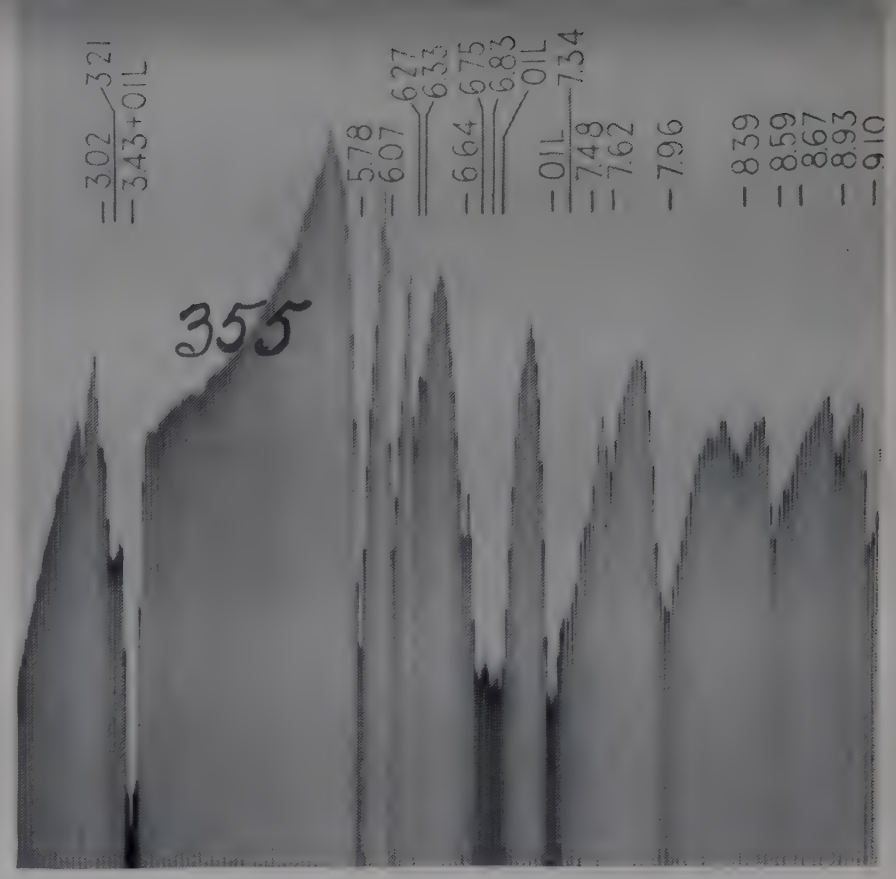


PLATE 206. 5.78 μ 4-C=O (ring); 6.07 μ C=C;
6.27 μ, 6.33 μ, 6.64 μ Conj. phenyl; 6.72 μ Thioureide ion.
Oil paste

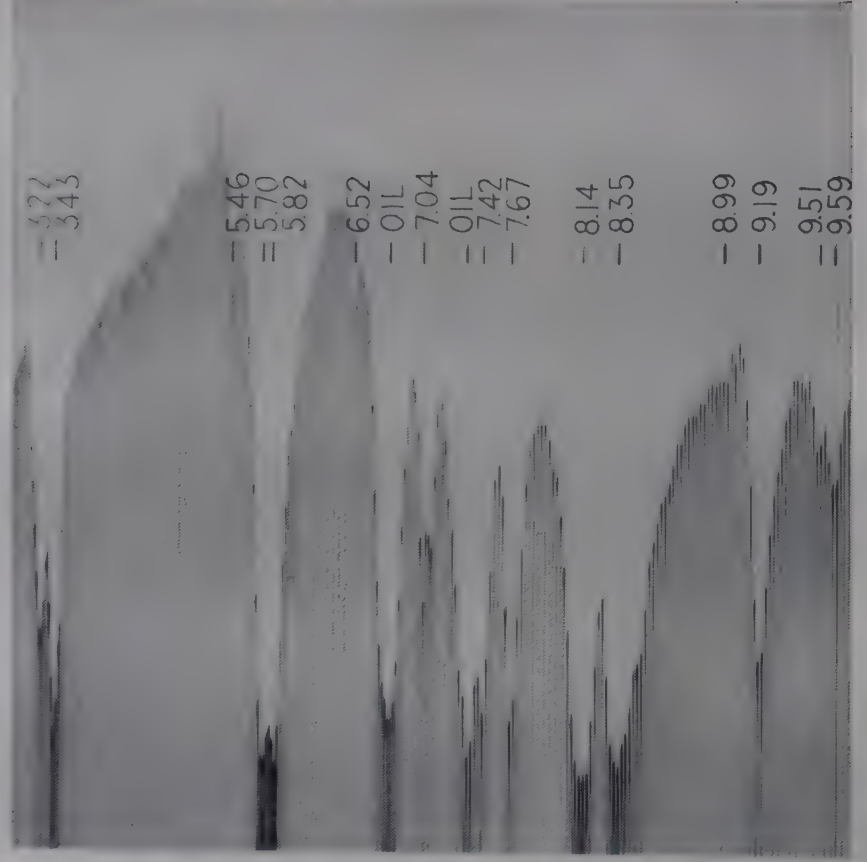


PLATE 207. Assignments: 5.70 μ 4-C=O
5.82 μ N-acyl C=O
6.81 μ Thioureide ion
Preparation: Oil paste

PLATE 207a. Assignments: 5.68 μ C=O
5.87 μ N-acyl C=O
Preparation: Pyridine solution, 0.02 mm.

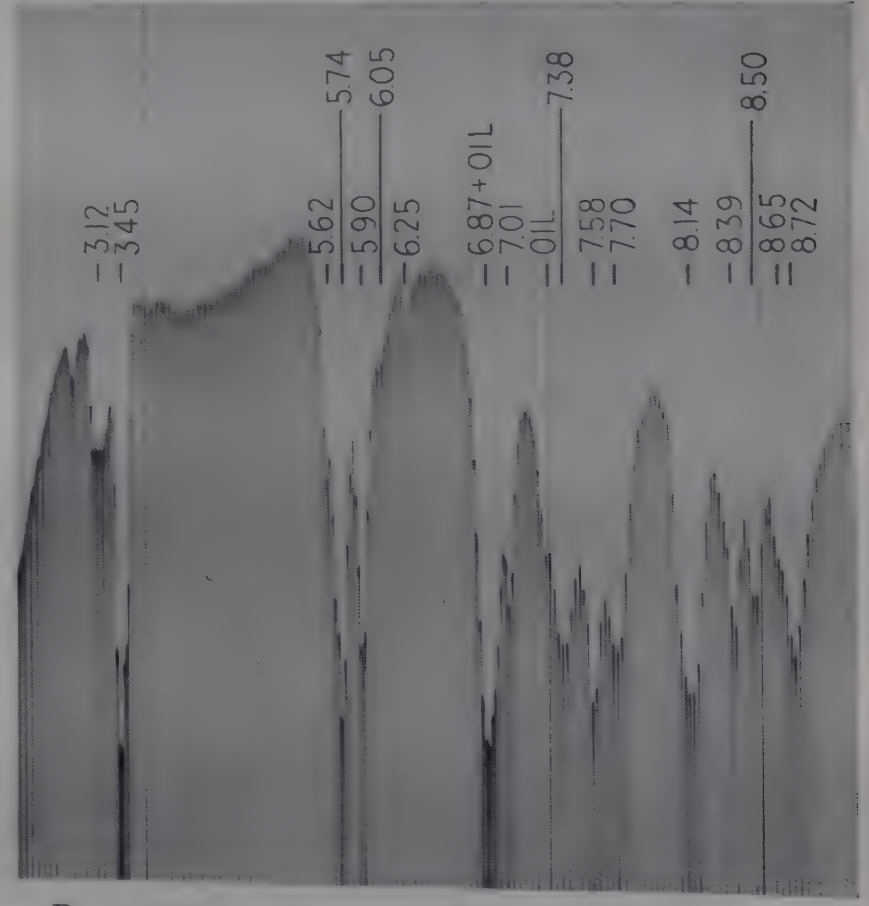


PLATE 208. Assignments: 5.74 μ 4-C=O
5.90 μ N-acyl C=O
6.87 μ Thioureide ion
Preparation: Oil paste

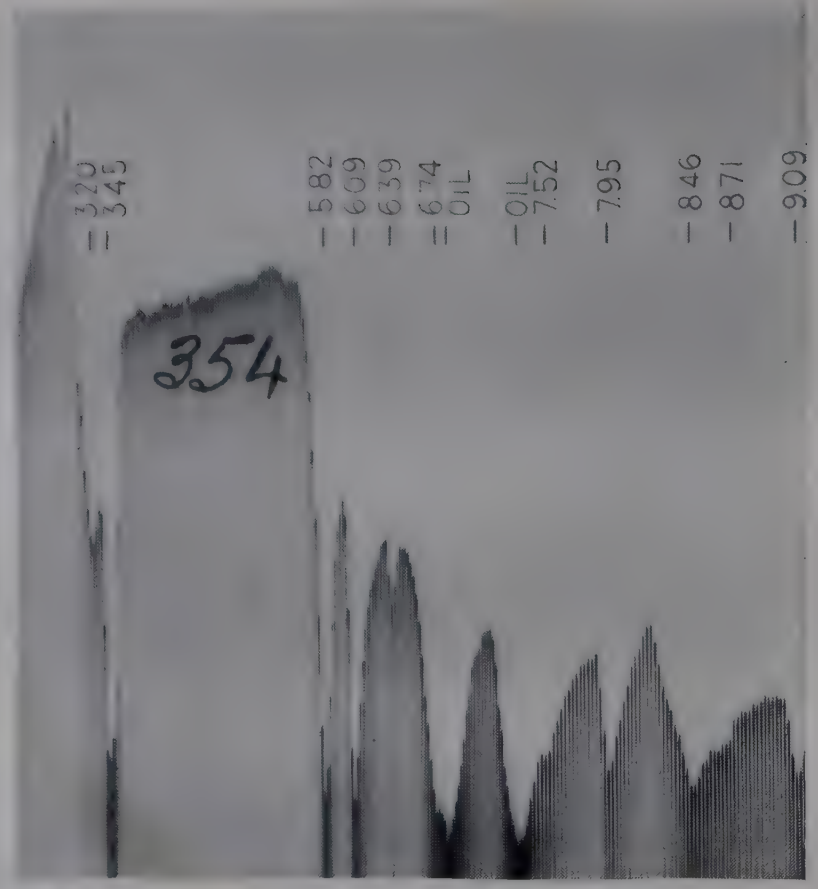
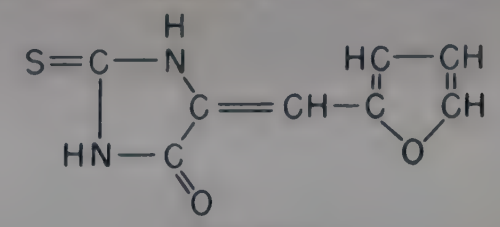


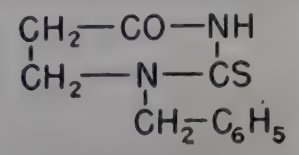
PLATE 209. Assignments: 5.82 μ 4-C=O
6.09 μ Ring C=N
6.74 μ Thioureide ion
Preparation: Oil paste

5-FURFURYLIDENE-2-THIOHYDANTOIN



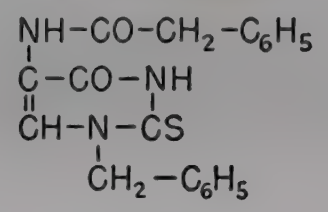
(Top Left)

1-BENZYL-5,6-DIHYDRO-2-THIOURACIL



(Top Right)

1-BENZYL-5-PHENACETAMIDO
2-THIOURACIL



(Bottom)

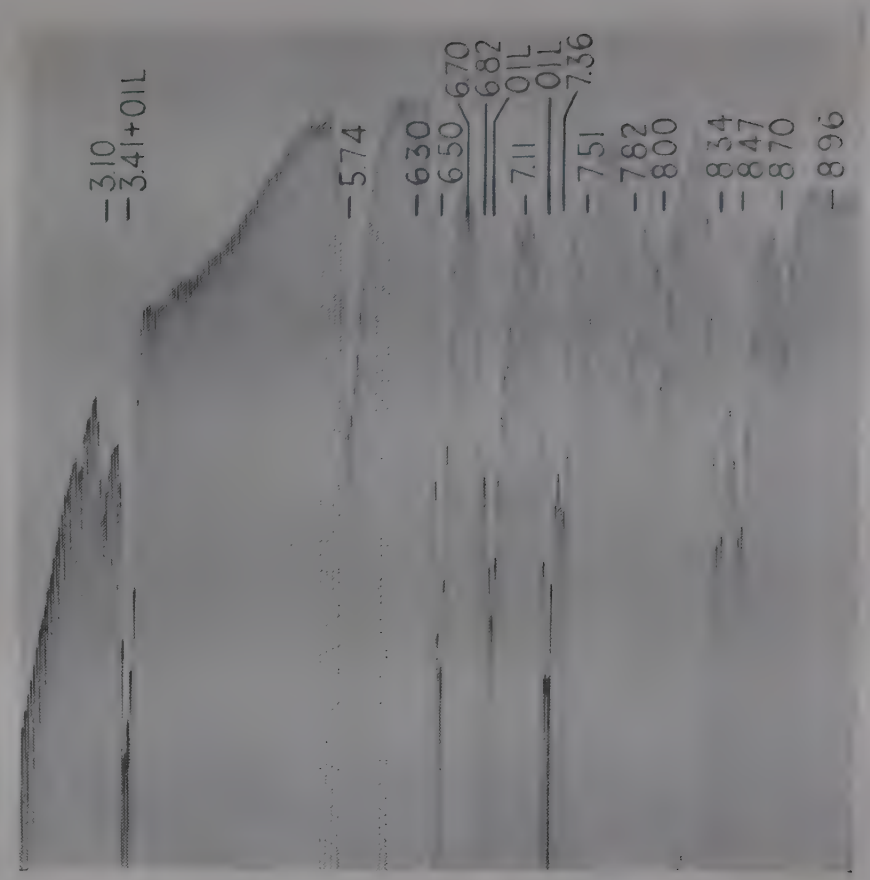


PLATE 212. Assignments: 5.74 μ 4-C=O (ring)
6.50 μ Thioureide ion
Preparation: Oil paste

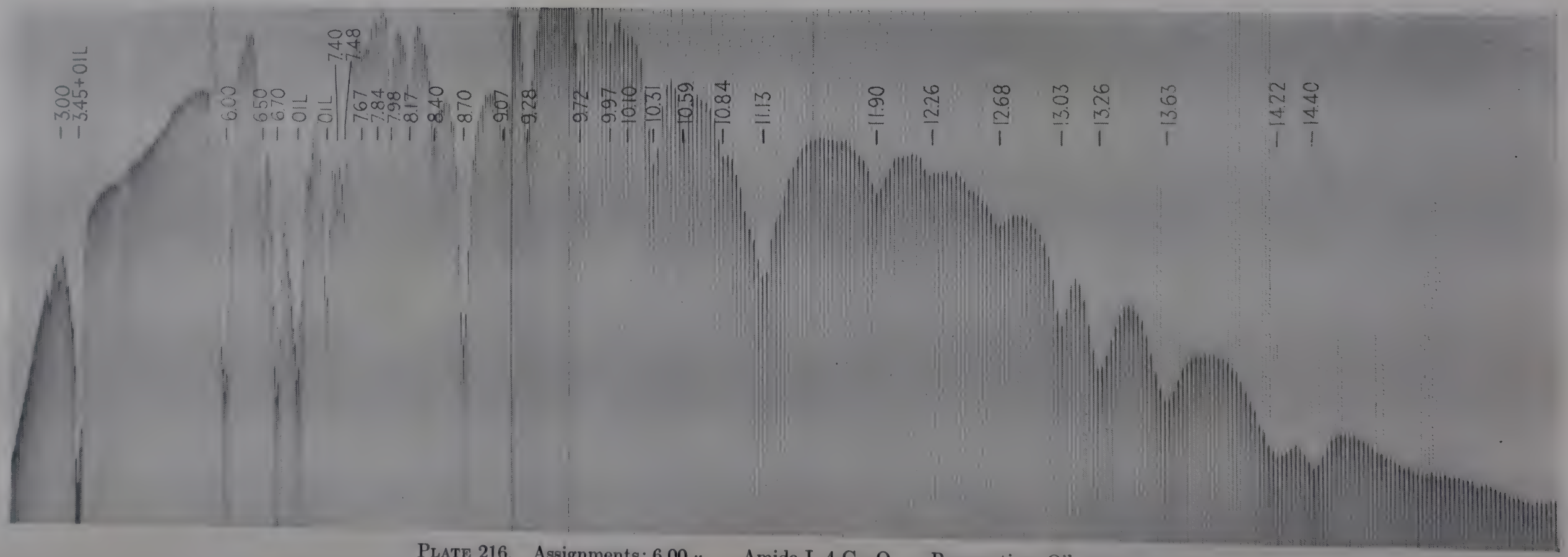


PLATE 216. Assignments: 6.00 μ Amide I, 4-C=O
6.50 μ Amide II
6.70 μ Thioureide ion
Preparation: Oil paste

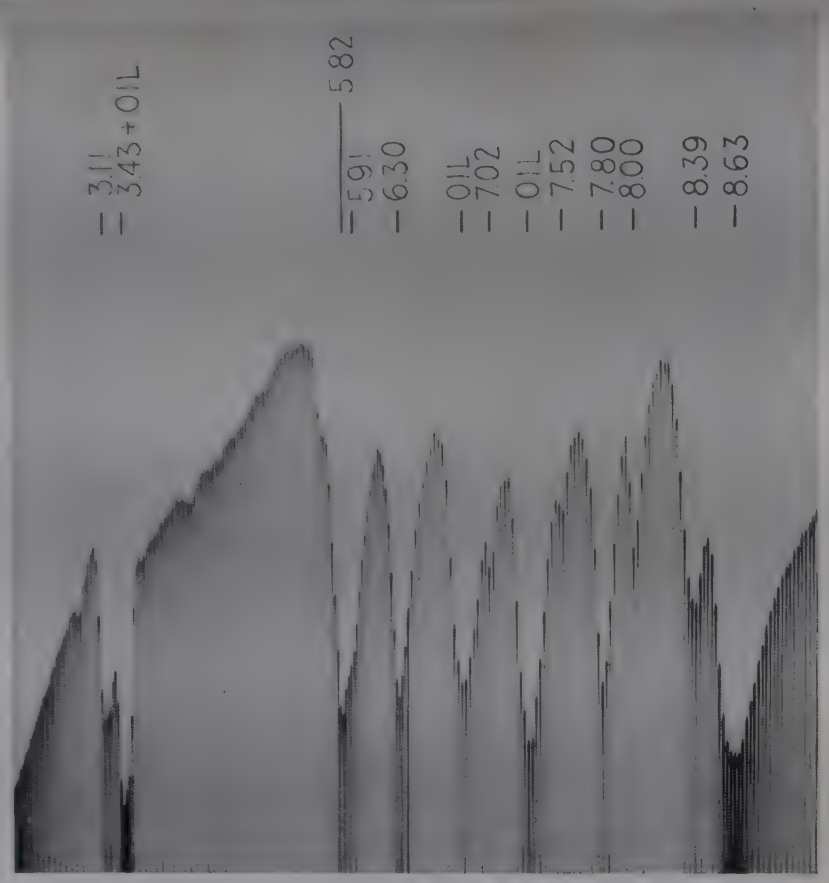
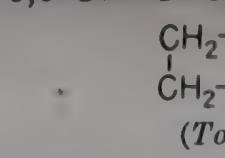


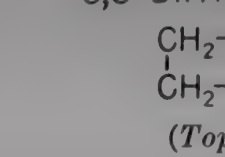
PLATE 213. Assignments: 5.82 μ 4-C=O
6.30 μ Thioureide ion
Preparation: Oil paste

5,6-DIHYDRO-2-THIOURACIL



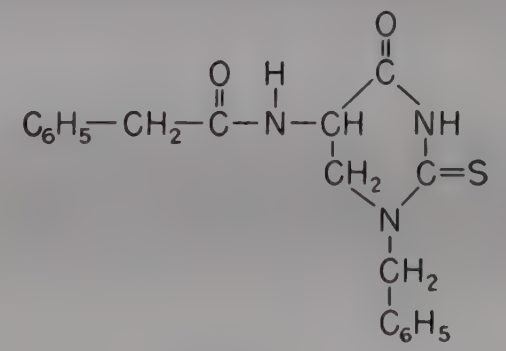
(*Top Left*)

5,6-DIHYDROURACIL



(*Top Right*)

1-BENZYL-5-PHENACETAMIDO-5,
6-DIHYDRO-2-THIOURACIL



(*Bottom*)

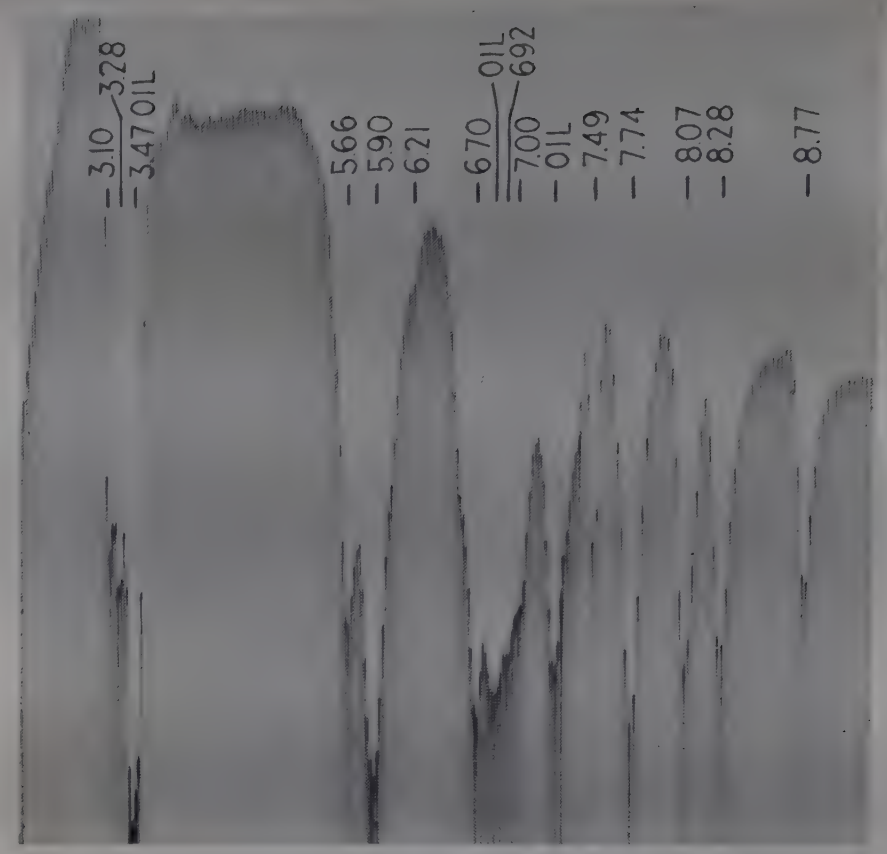


PLATE 214. Assignments: 5.66 μ 4-C=O
5.90 μ 2-C=O
Preparation: Oil paste

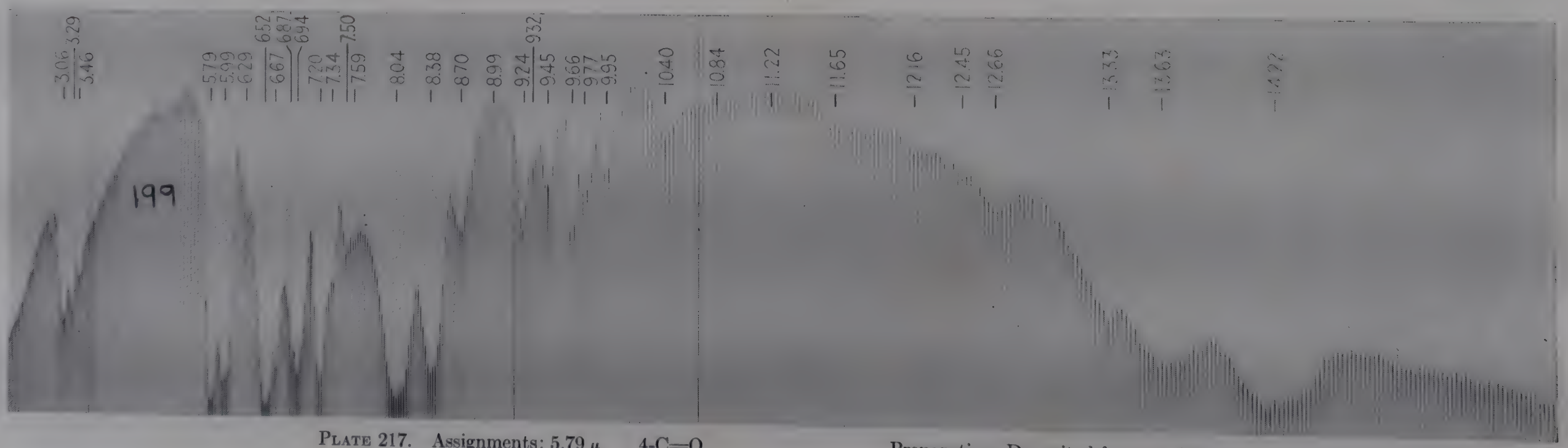


PLATE 217. Assignments: 5.79 μ 4-C=O
5.99 μ Amide I
6.52 μ Amide II, thioureide ion
Preparation: Deposited from pyridine

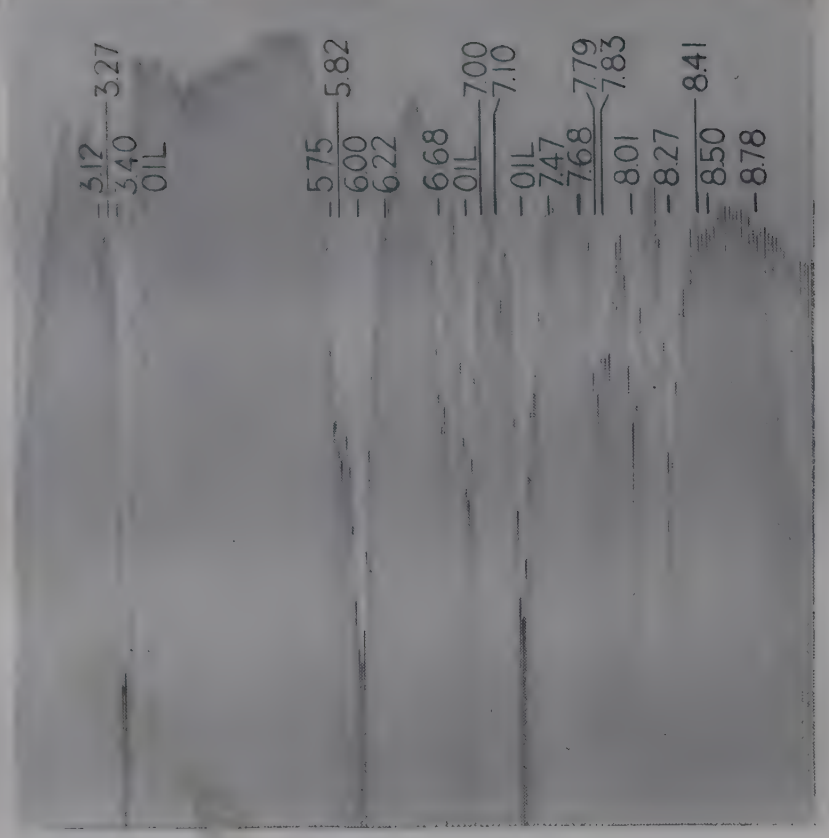
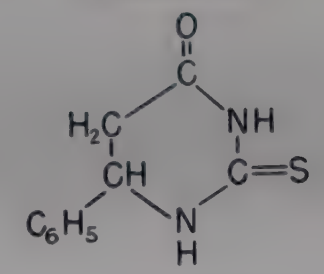


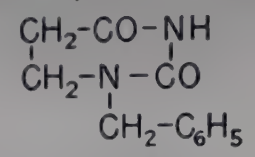
PLATE 215. Assignments: 5.82 μ 4-C=O
6.00 μ 2-C=O
Preparation: Oil paste

6-PHENYL-5,6-DIHYDRO-2-THIOURACIL



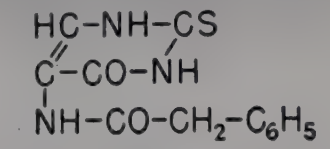
(Top Right)

1-BENZYL-5,6-DIHYDROURACIL



(Top Left)

5-PHENACETAMIDO-2-THIOURACIL



(Bottom)

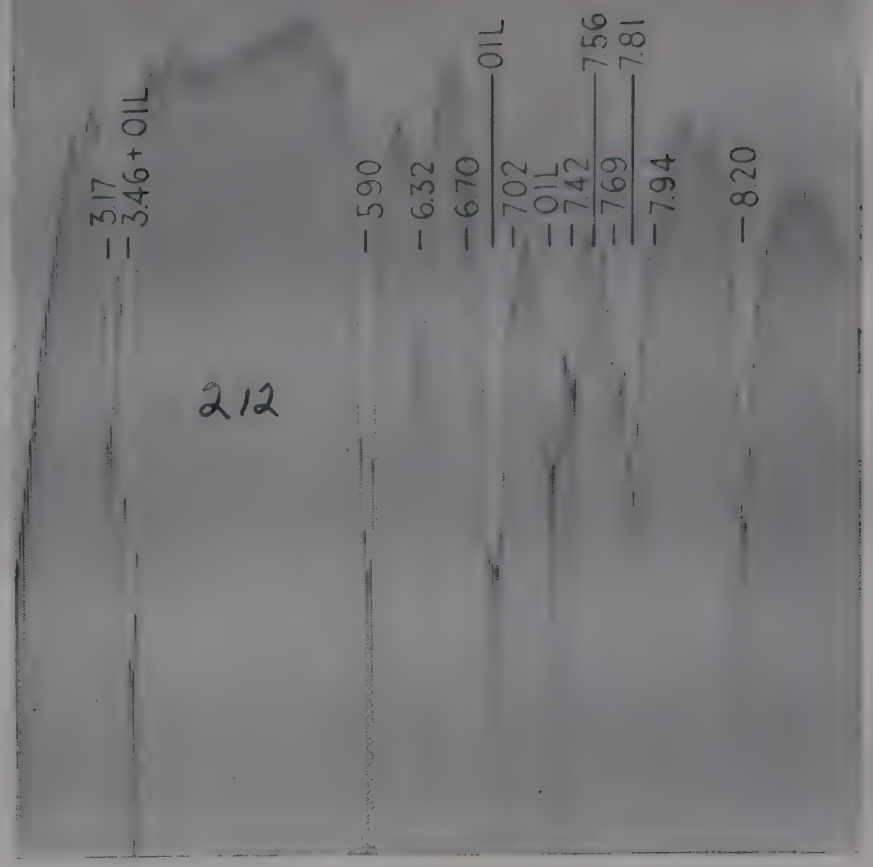


PLATE 219. Assignments: 5.90 μ 4-C=O
6.32 μ Thioureide ion
Preparation: Oil paste

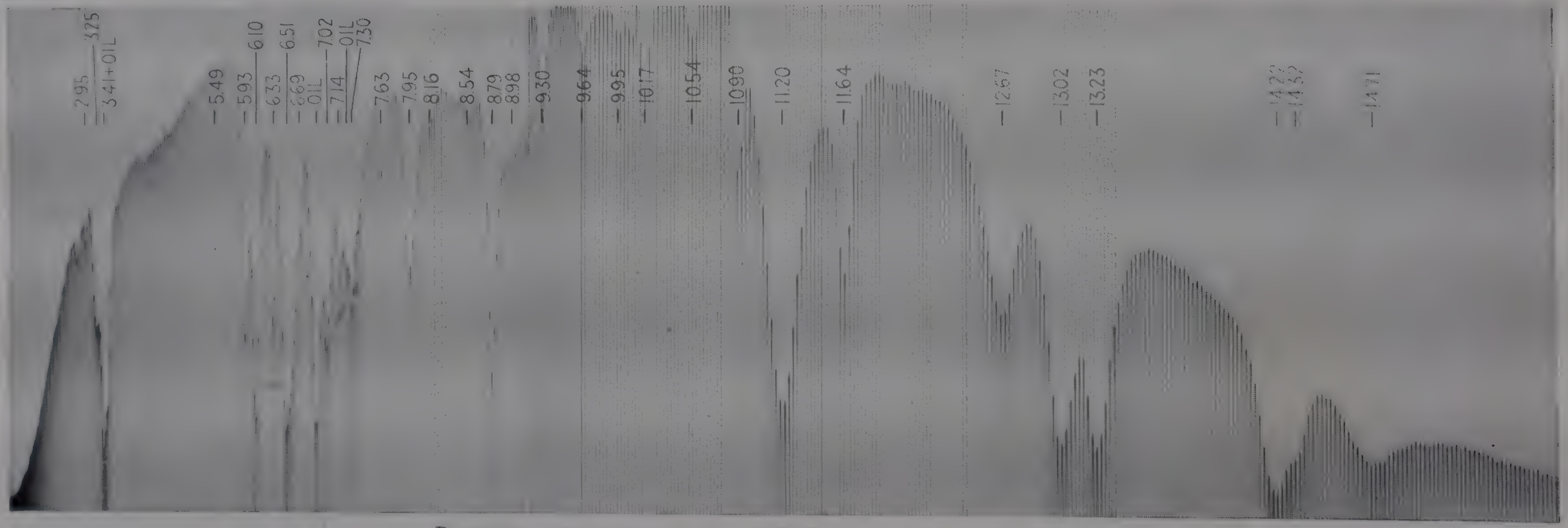


PLATE 218. Assignments: 5.93 μ 4-C=O
6.10 μ Amide I
6.33 μ Thioureide ion
6.51 μ Amide II
Preparation: Oil paste

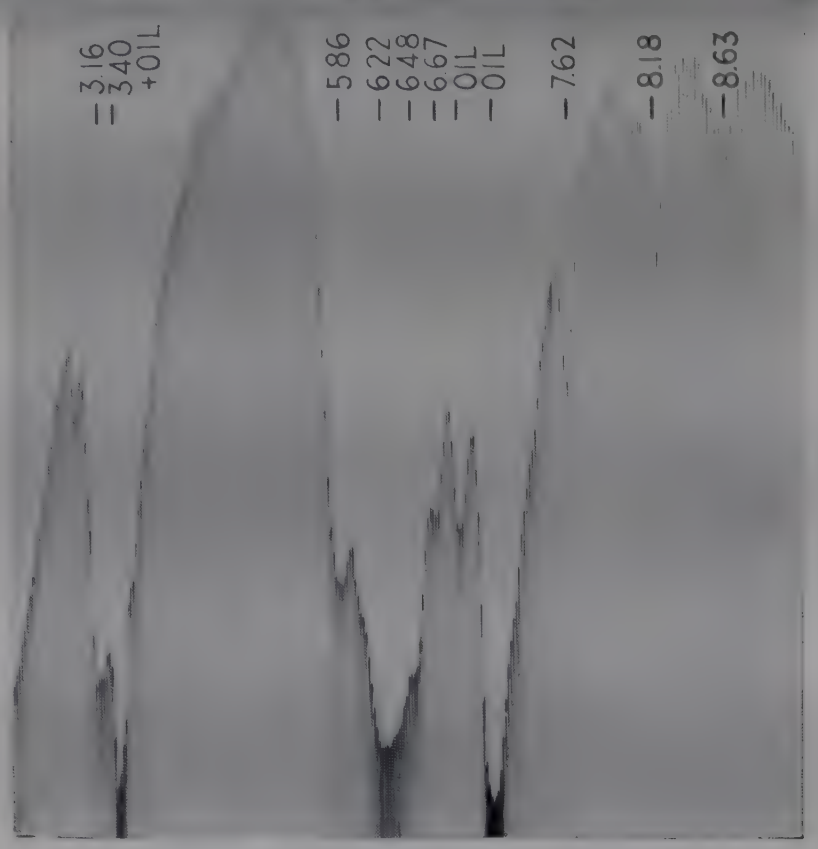
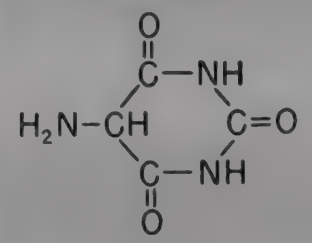


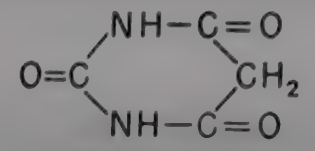
PLATE 220. Preparation: Oil paste

URAMIL



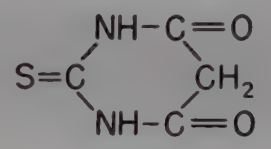
(*Top Left*)

BARBITURIC ACID



(*Top Right*)

2–THIOBARBITURIC ACID



(*Bottom*)

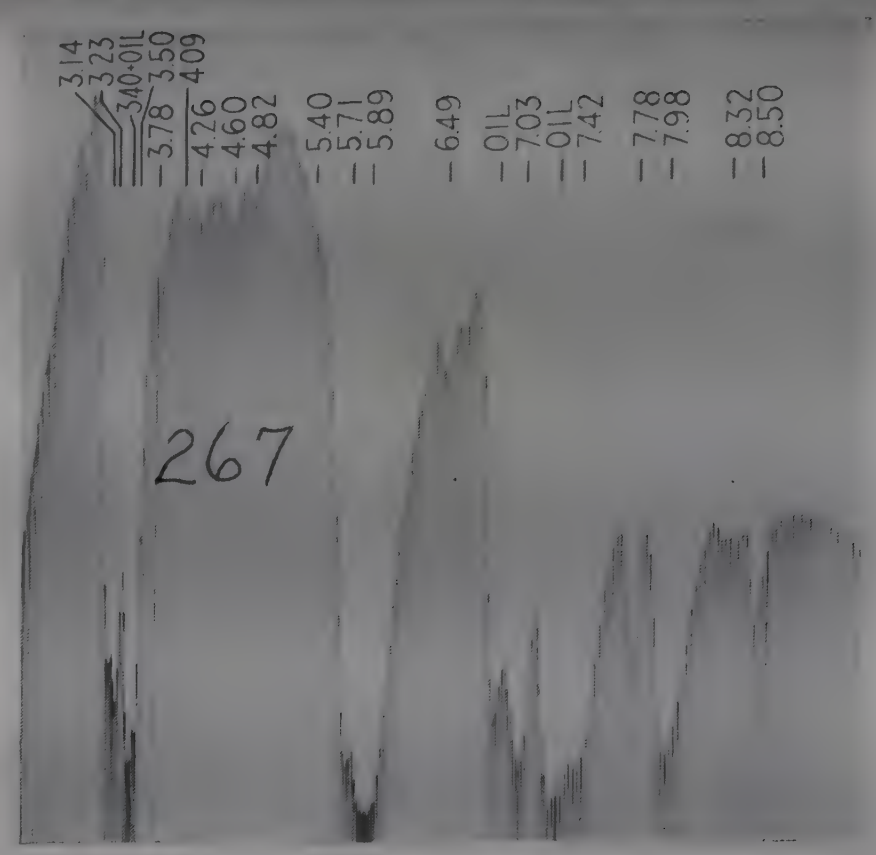


PLATE 221. Preparation: Oil paste

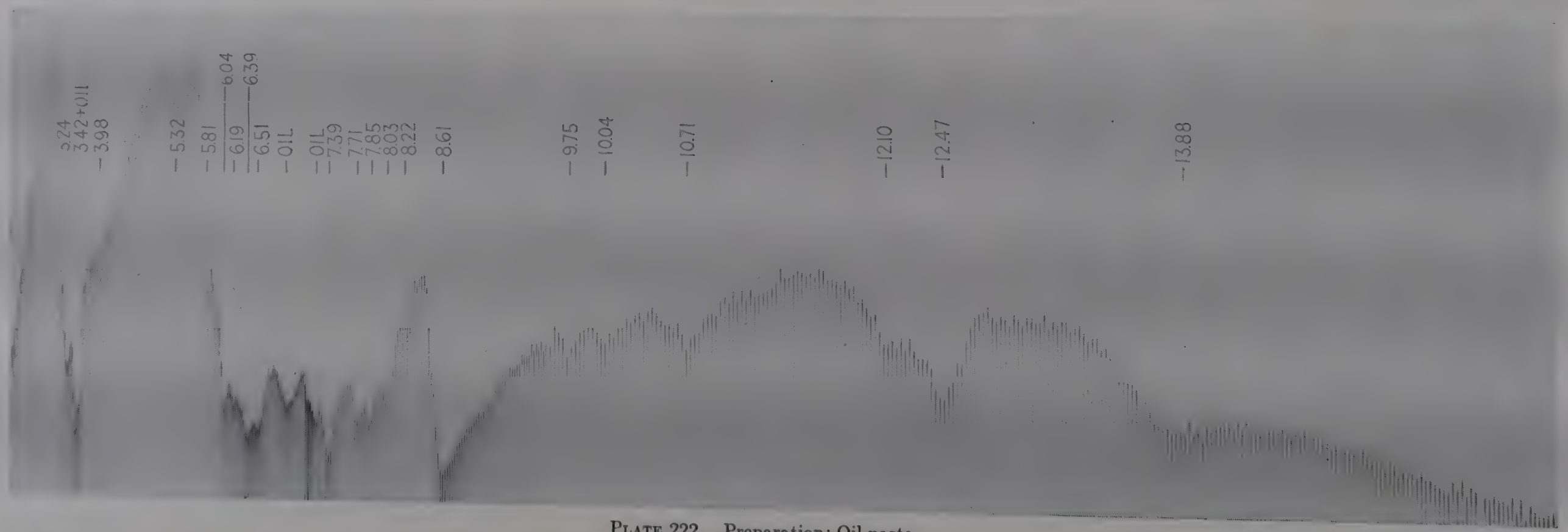


PLATE 222. Preparation: Oil paste

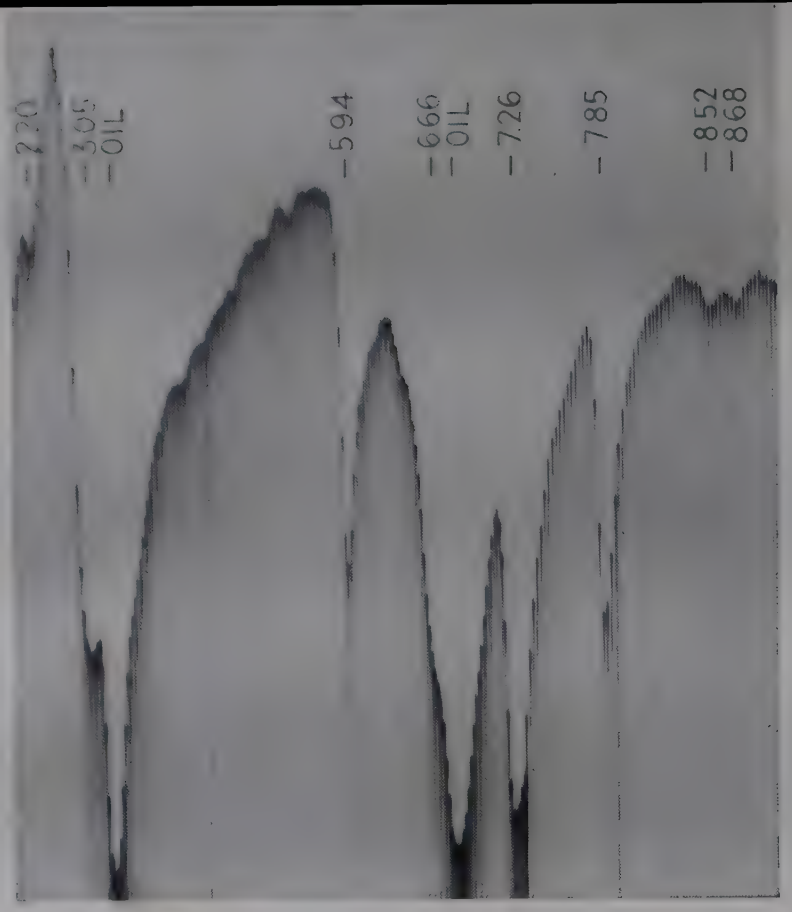
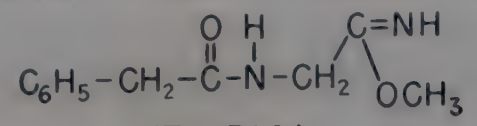


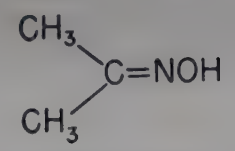
PLATE 225. Assignments: 5.94 μ C=N
6.66 μ Unassigned
Preparations: Oil paste

PHENACETURIMINOMETHYLETHER
(METHYL PHENACETURIMIDATE)



(Top Right)

ACETOXIME



(Top Left)

ALLOXANTIN
(Bottom)

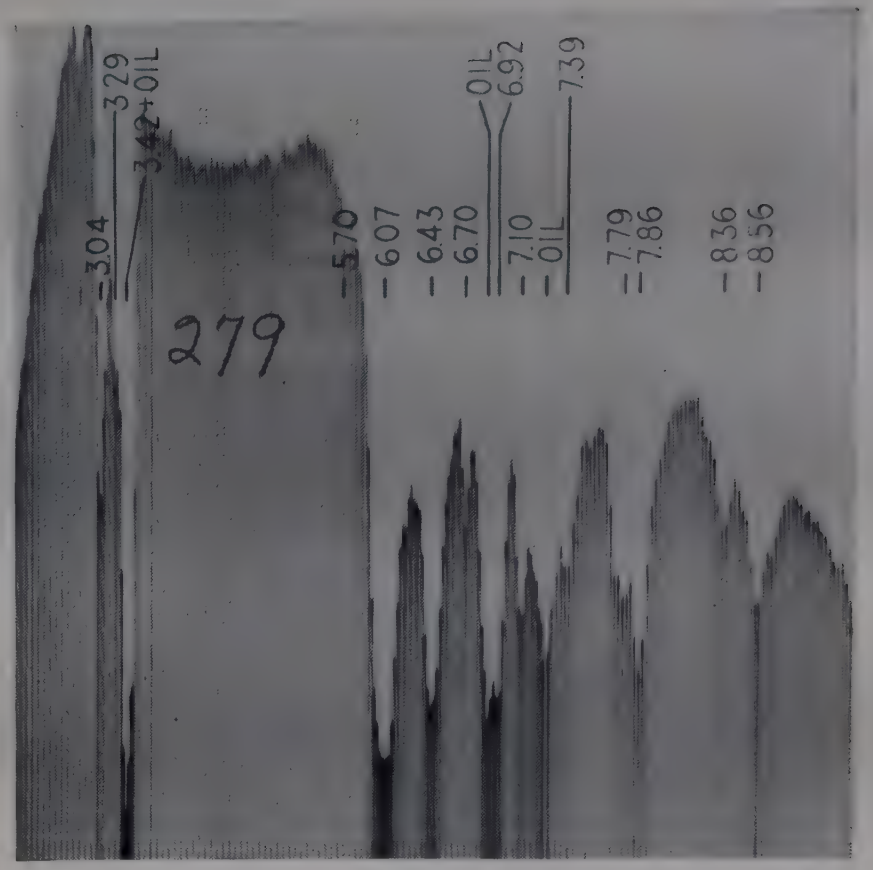


PLATE 226. Assignments: 6.07 μ C=N, Amide I
6.43 μ Amide II
Preparations: Oil paste

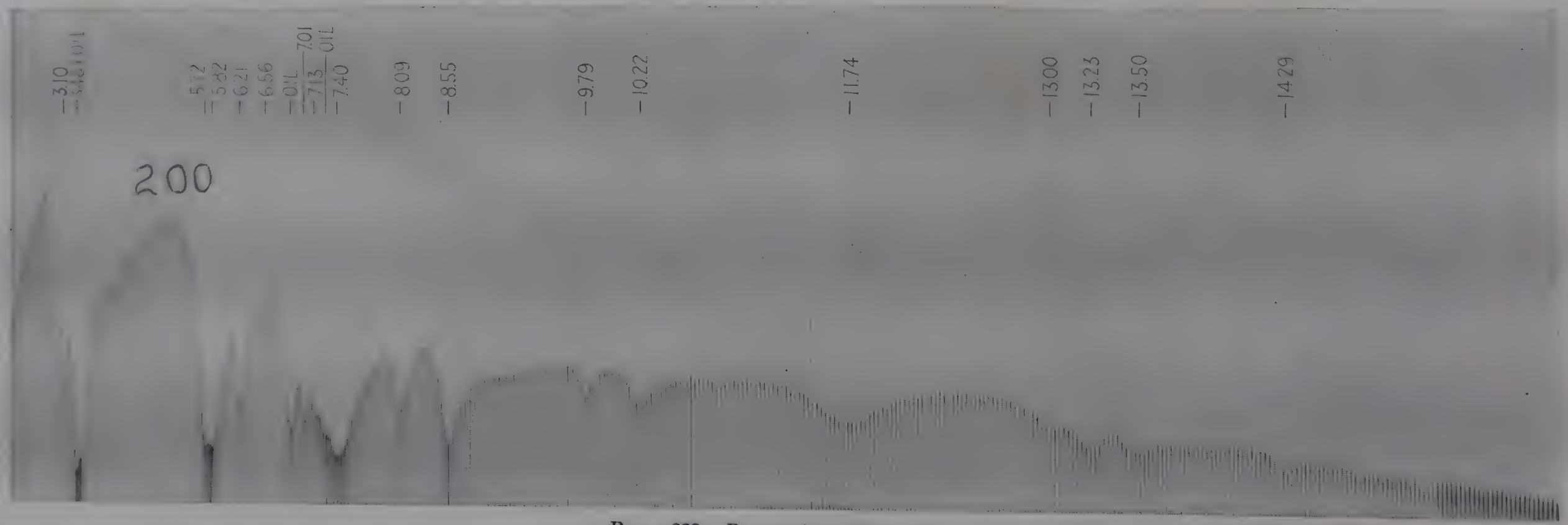
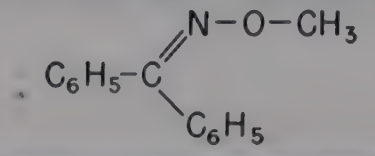


PLATE 223. Preparations: Oil paste

O-METHYLBENZOPHENOXIME



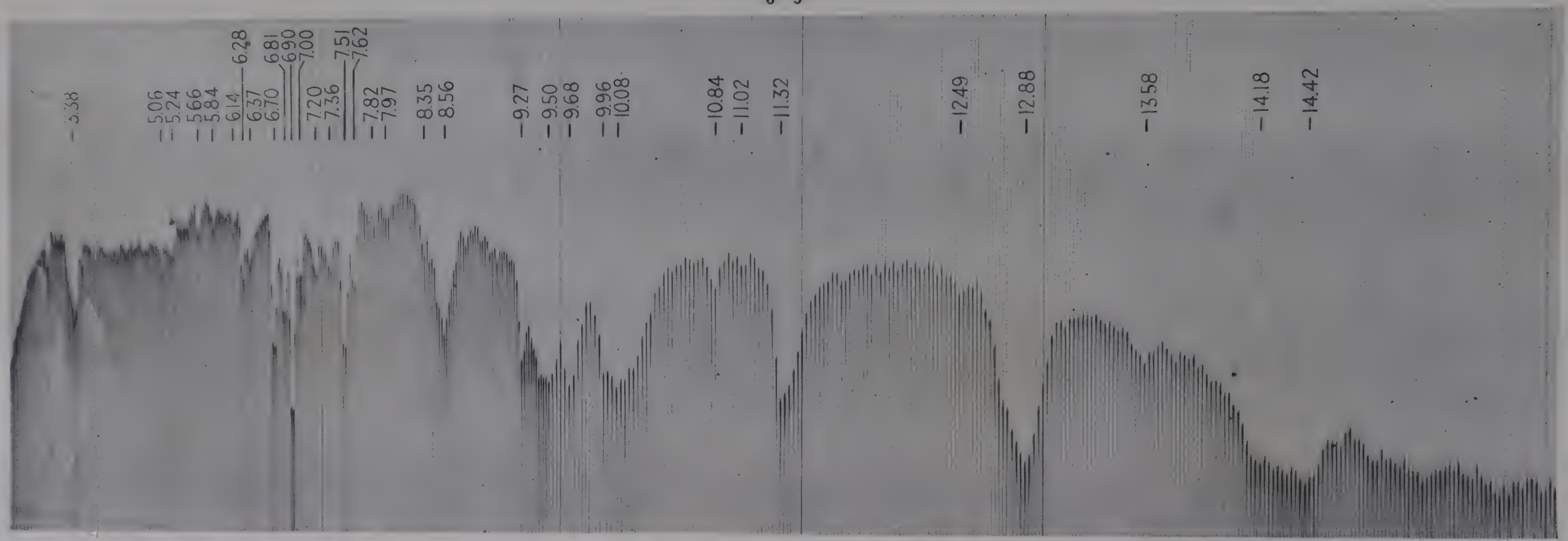
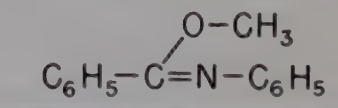


PLATE 224. Preparations: Melted and solidified

METHYL N-PHENYLBENZAMIDATE



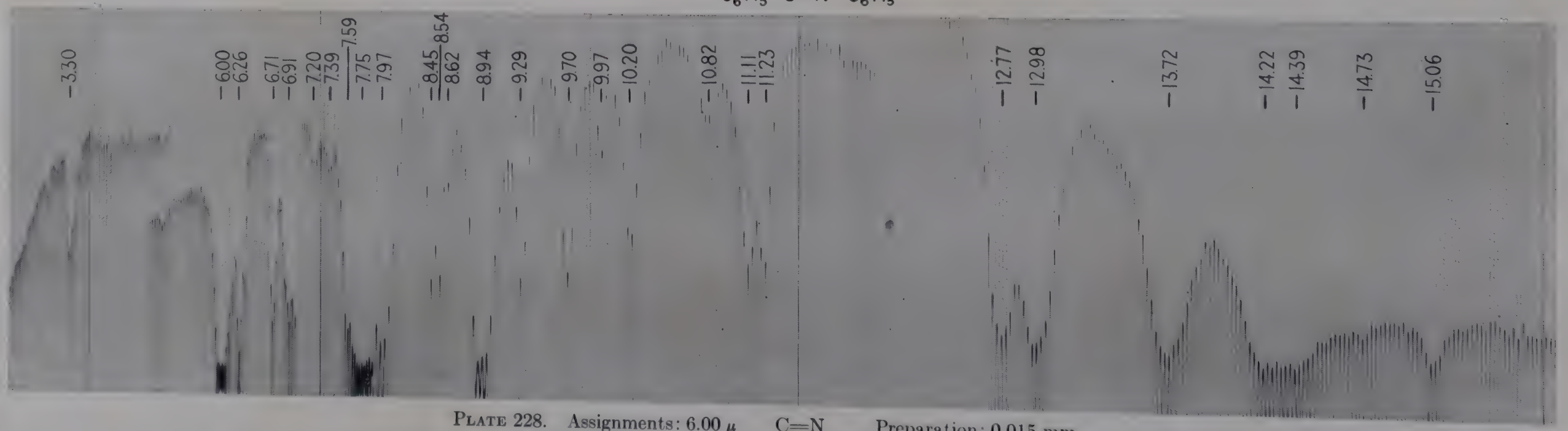


PLATE 228. Assignments: 6.00 μ C=N; 6.26 μ, 6.71 μ Phenyl. Preparation: 0.015 mm.

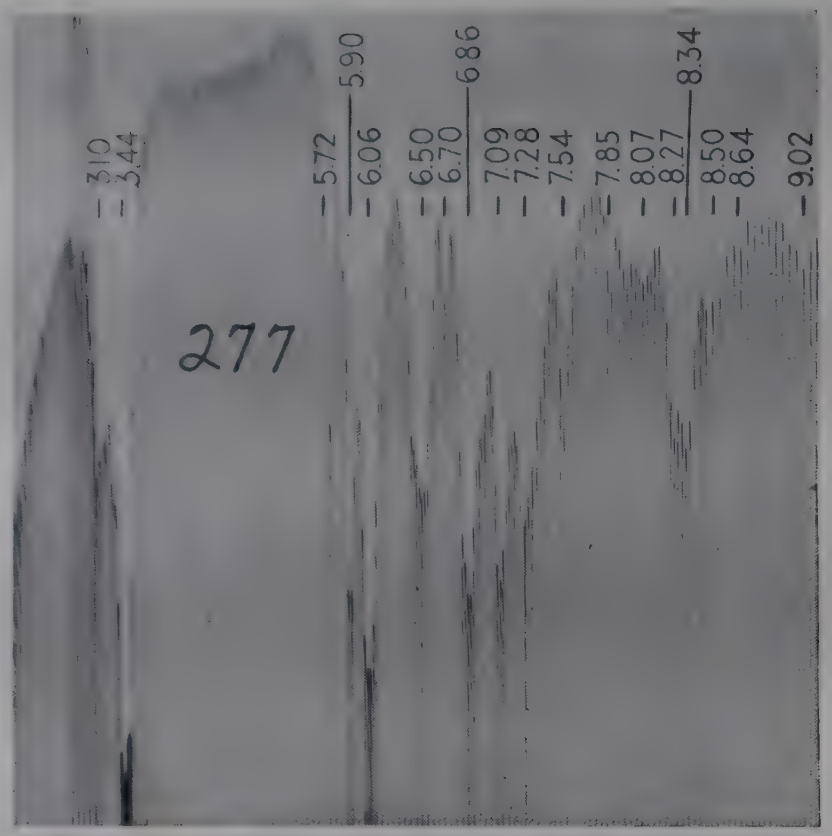
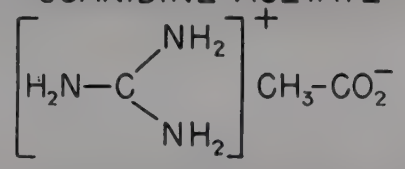


PLATE 227. Assignments: 5.90 μ $C{=}N^+$
6.06 μ Amide I
6.50 μ Amide II
Preparations: Oil paste

PHENACETURIMINOMETHYLETHER HYDROCHLORIDE
(Top Left)

GUANIDINE ACETATE



(Top Right and Bottom)

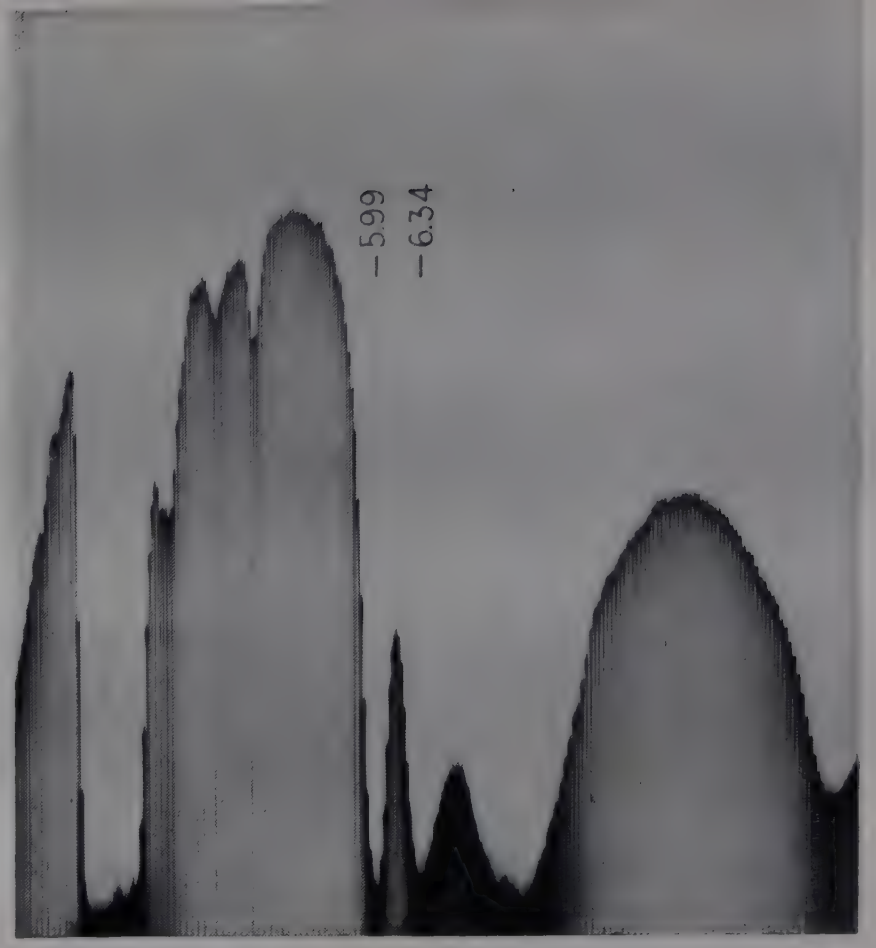


PLATE 229a. Assignments:
Bands not measured—Methanol
Preparation: Methanol solution, 0.02 mm.

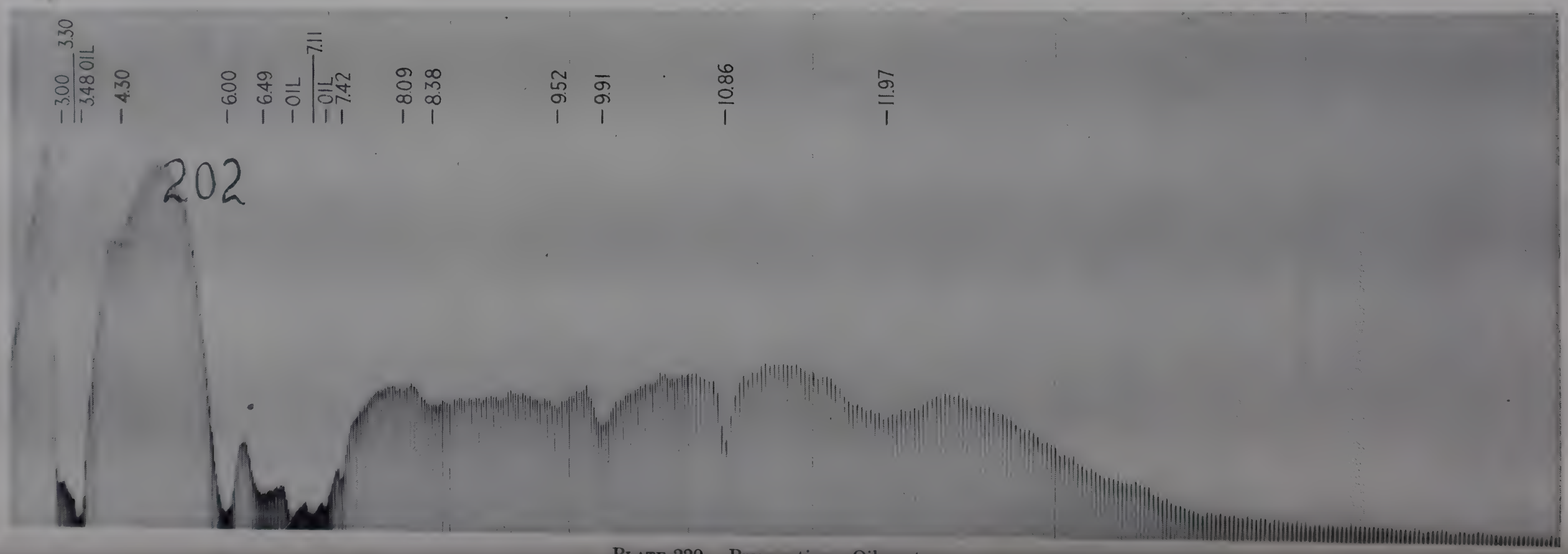
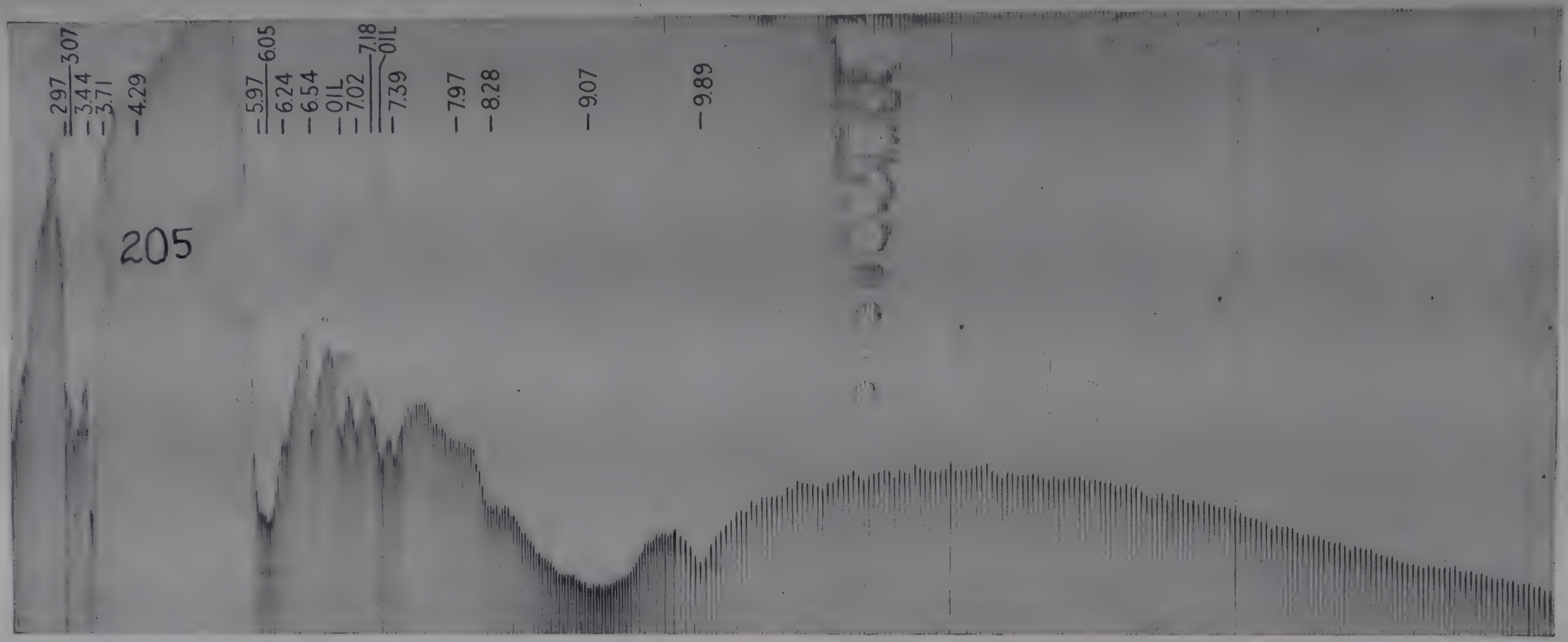


PLATE 229. Preparations: Oil paste



AMINOGUANIDINE SULPHATE

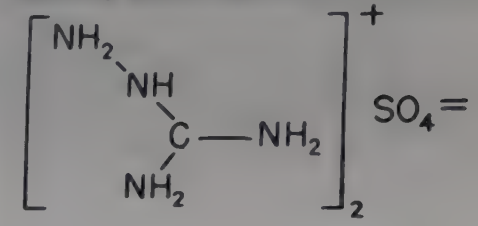
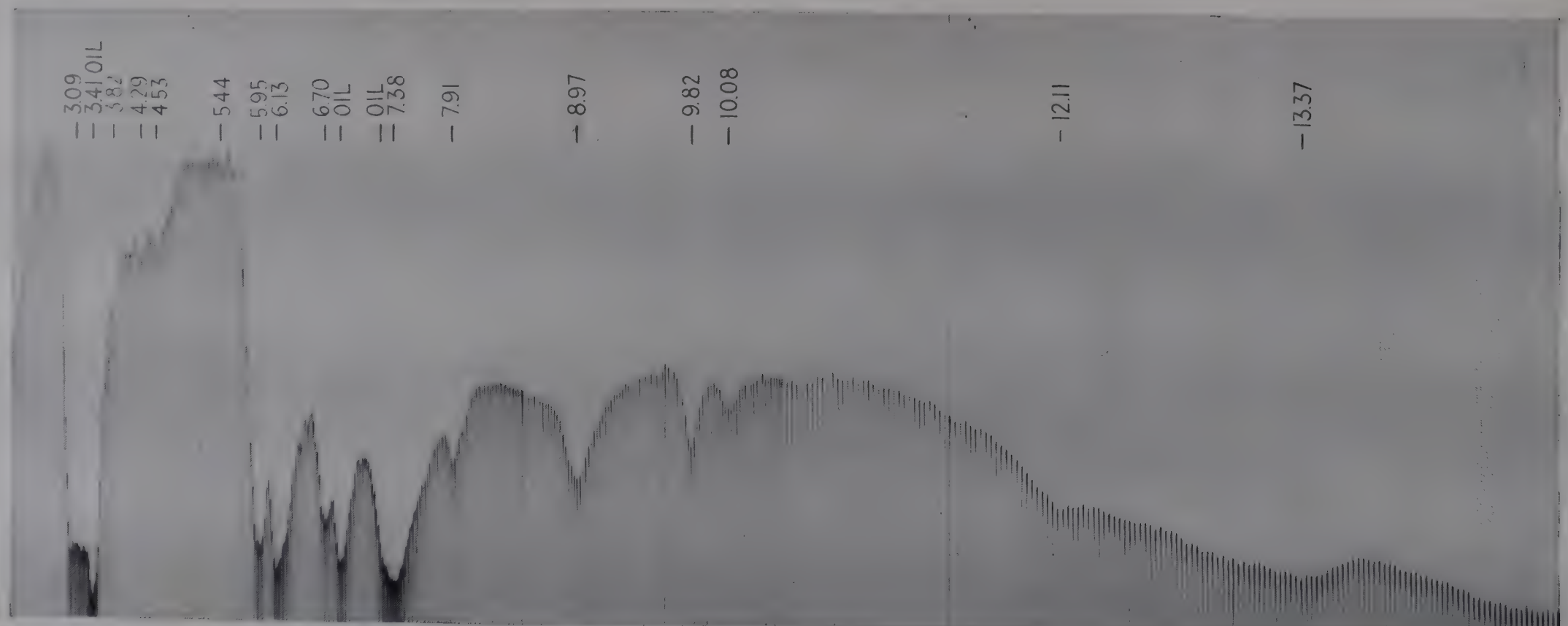


PLATE 230. Preparations: Oil paste



AMINOGUANIDINE BICARBONATE

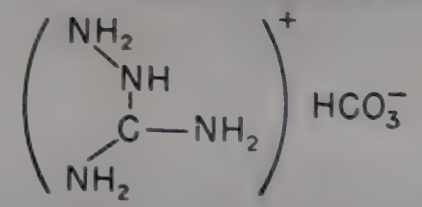
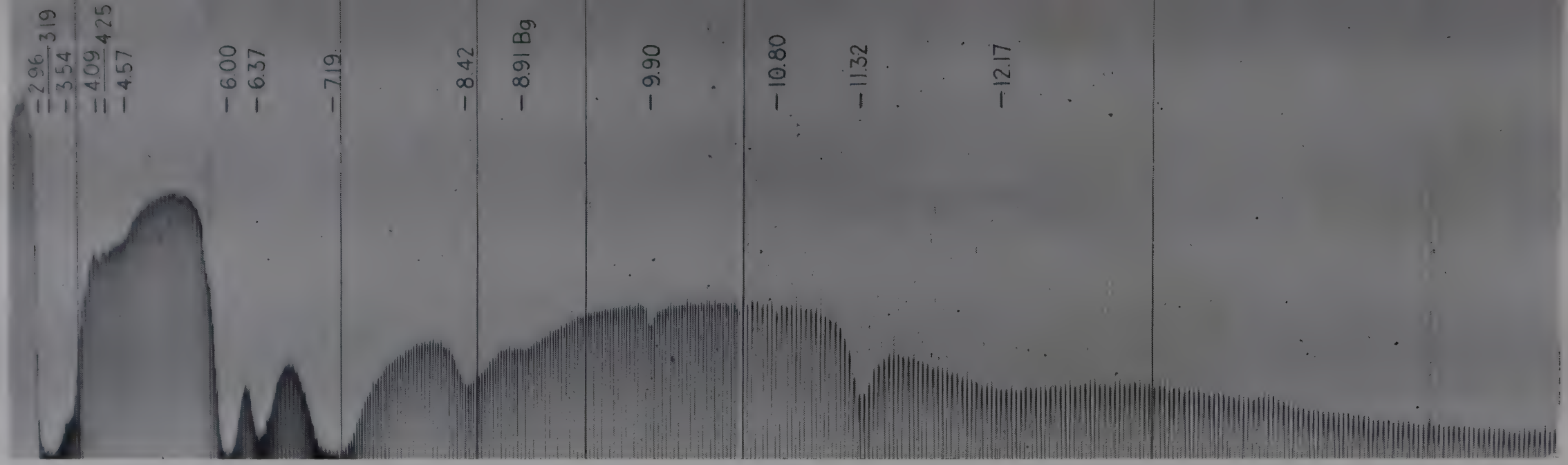


PLATE 231. Preparations: Oil paste



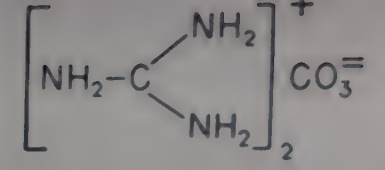
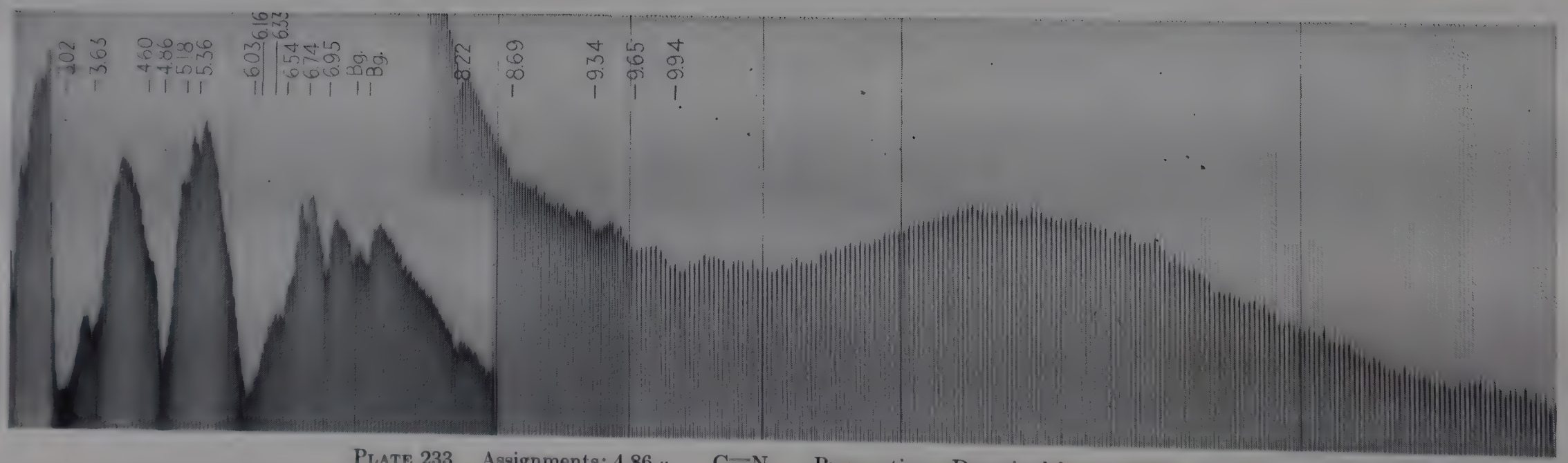


PLATE 232. Preparations: Deposited from water



GUANIDINE THIOCYANATE

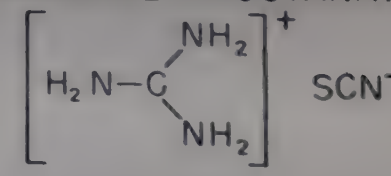


PLATE 233. Assignments: 4.86 μ C≡N Preparations: Deposited from pyridine

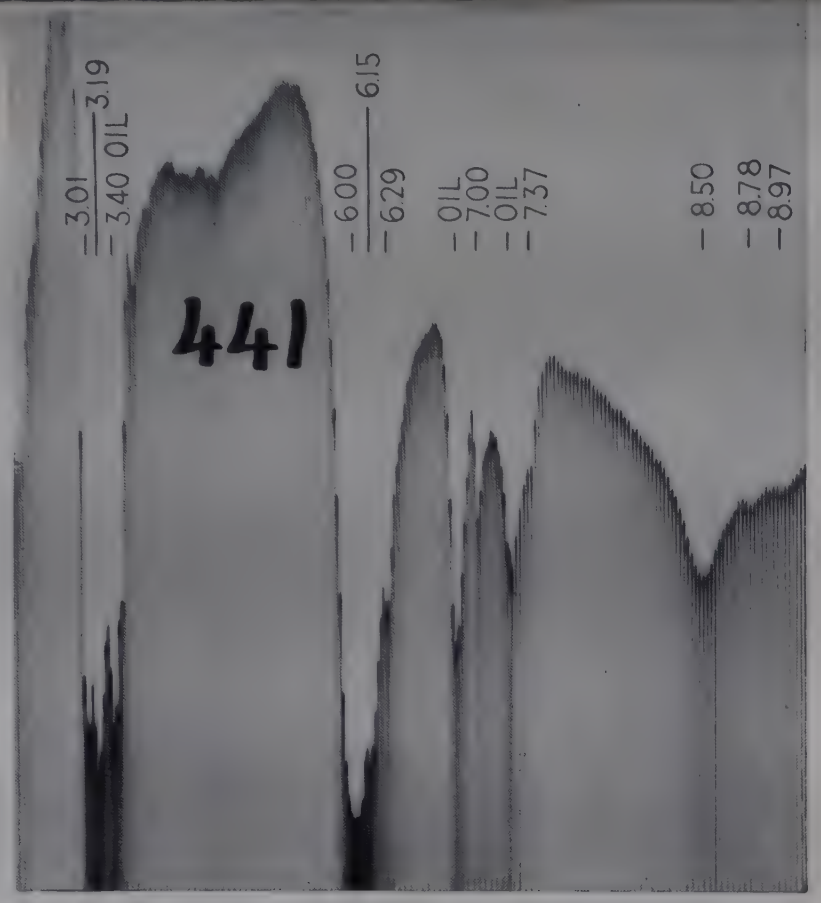
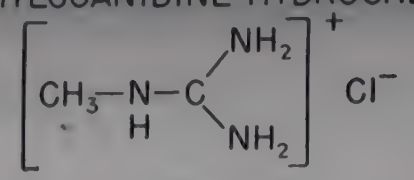


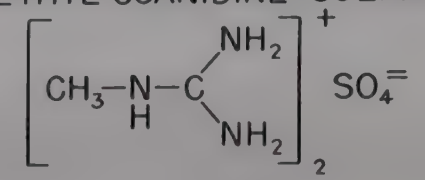
PLATE 235. Preparations: Oil paste

METHYLGUANIDINE HYDROCHLORIDE



(Top Left)

METHYL GUANIDINE SULPHATE



(Top Right)

AMMONIUM THIOCYANATE

$(NH_4)^+(NCS)^-$

(Bottom)

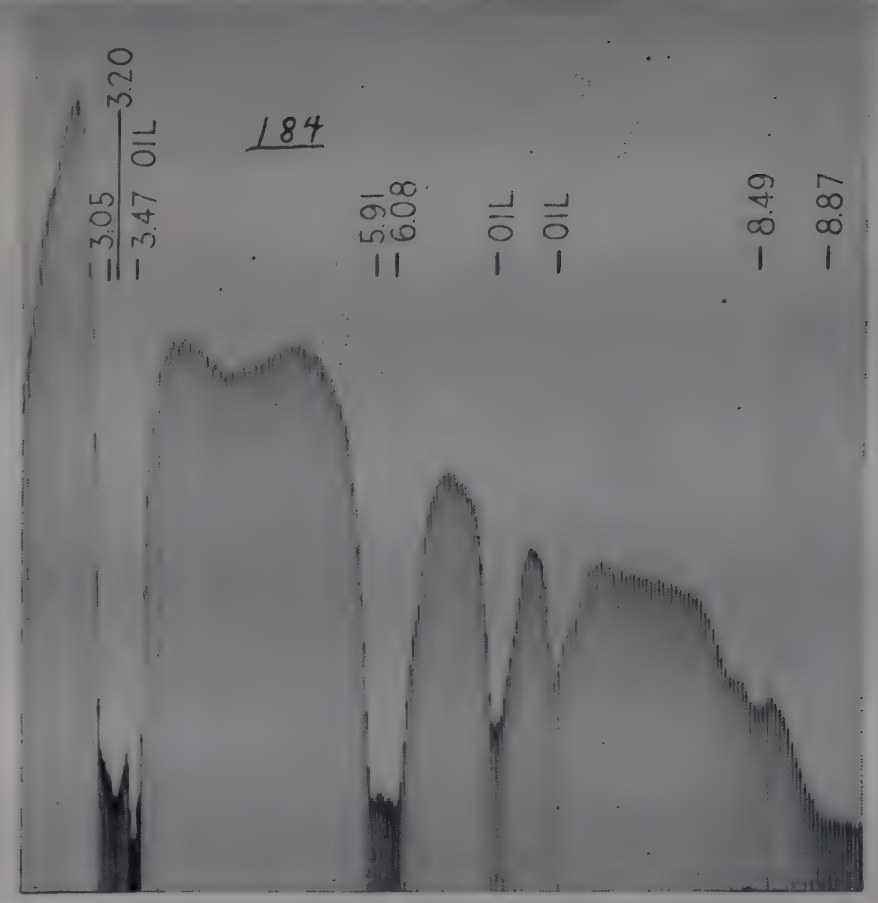


PLATE 236. Preparations: Oil paste

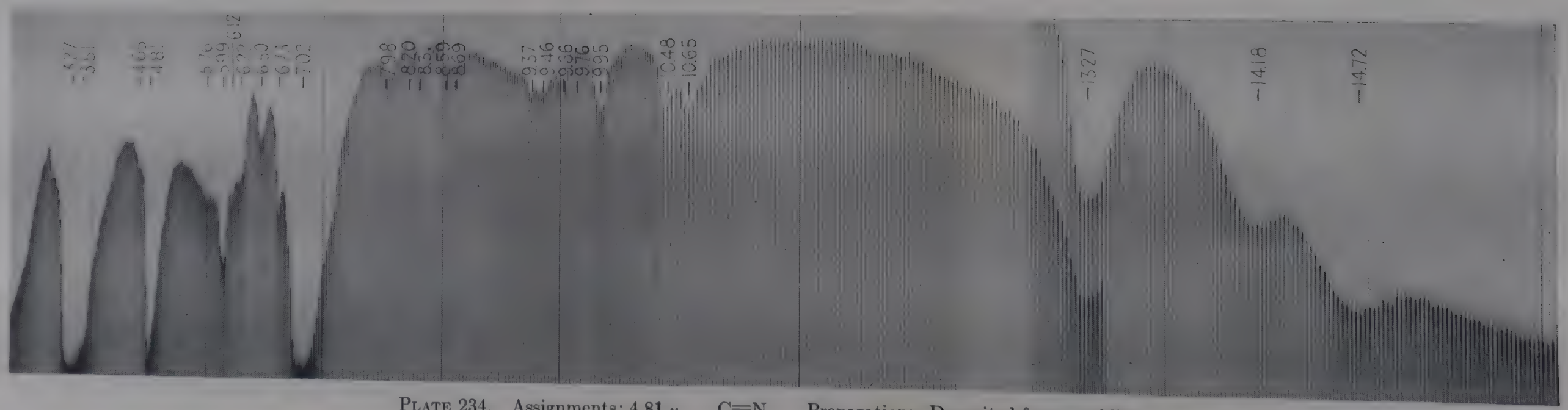


PLATE 234. Assignments: 4.81 μ C≡N Preparations: Deposited from pyridine

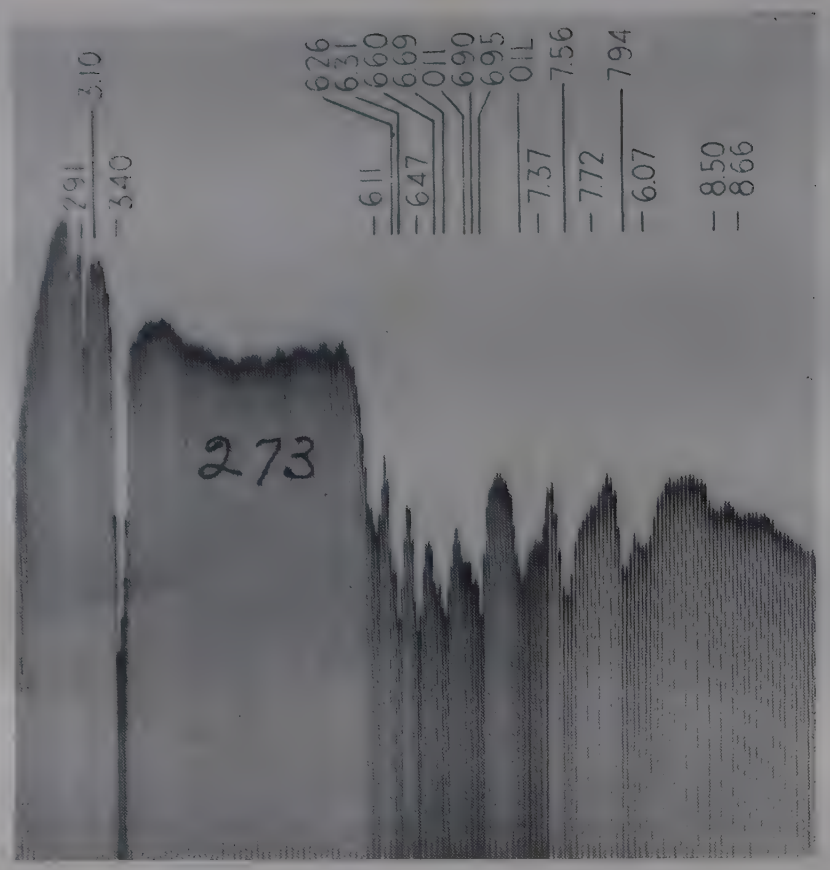
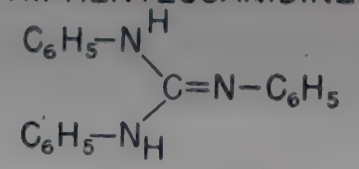


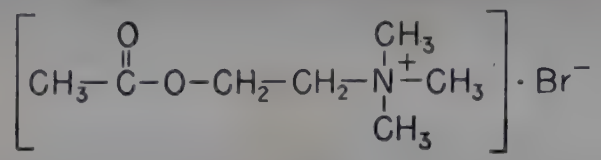
PLATE 237. Preparations: Oil paste

TRIPHENYLGUANIDINE



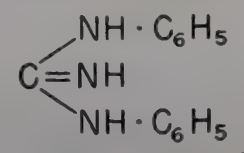
(Top Left)

ACETYLCHOLINE BROMIDE



(Top Right)

SYM–DIPHENYLGUANIDINE



(Bottom)

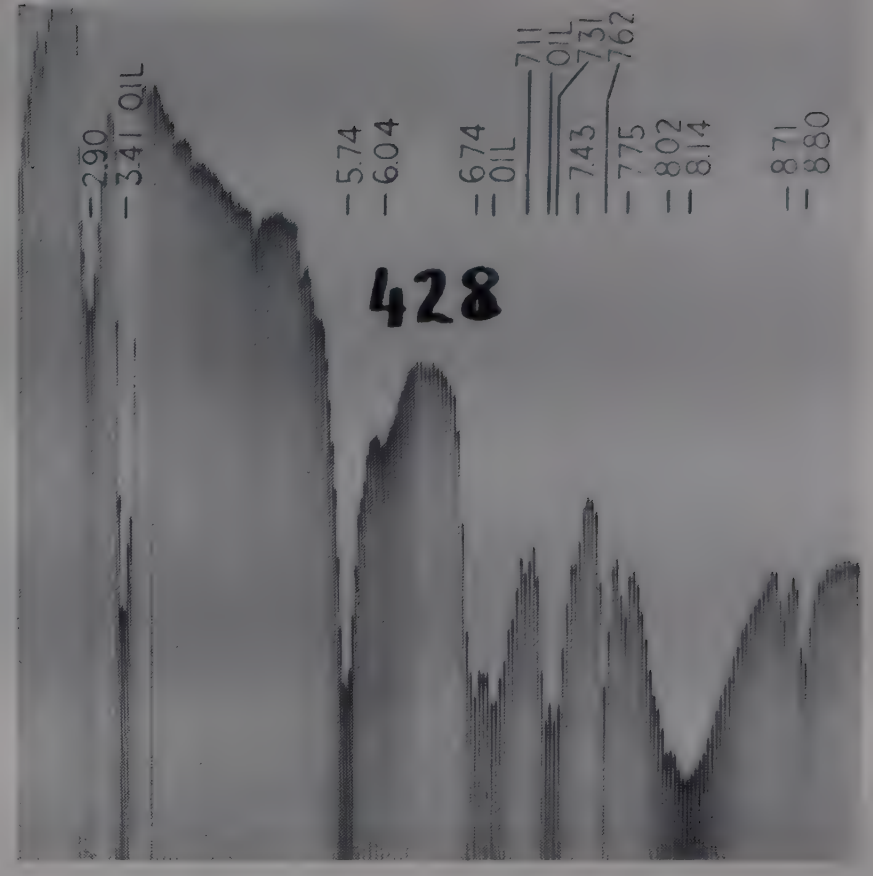


PLATE 239. Assignments: 5.74 μ Ester C=O
Preparations: Oil paste

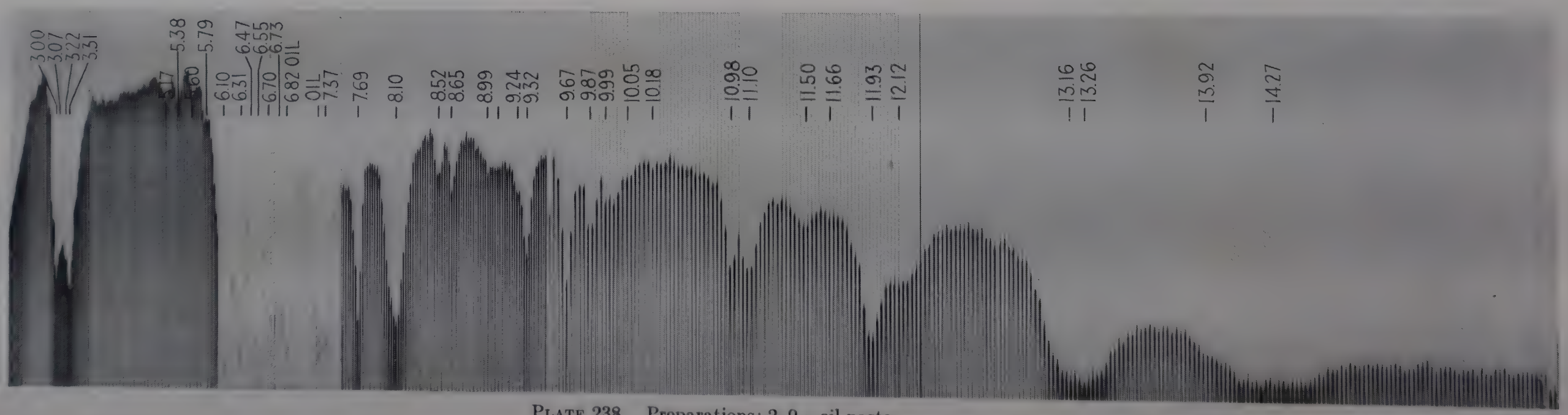


PLATE 238. Preparations: 2–9 μ oil paste
9–15 μ deposited from pyridine

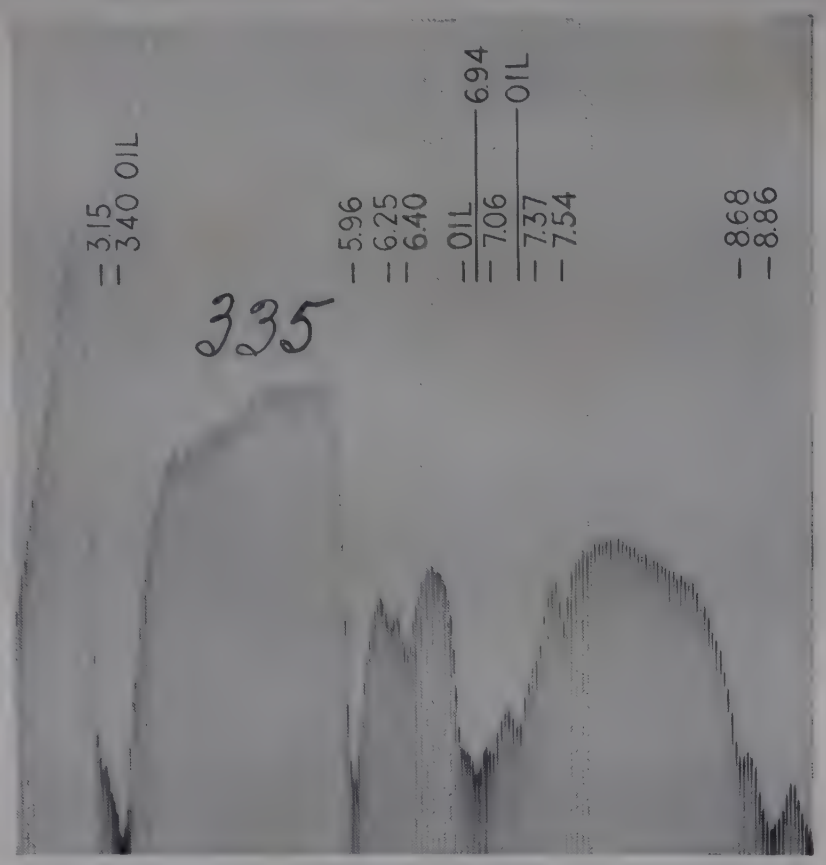
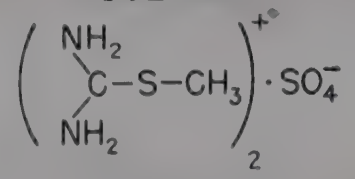


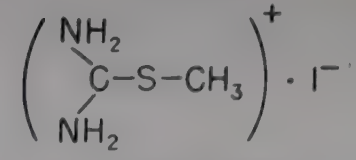
PLATE 240. Preparations: Oil paste

S-METHYLTHIOURONIUM SULPHATE



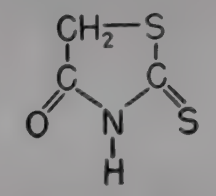
(Top Left)

S-METHYLTHIOURONIUM IODIDE



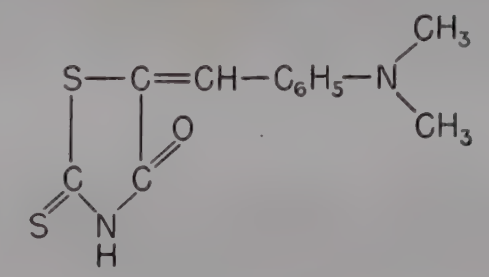
(Top Right)

RHODANINE



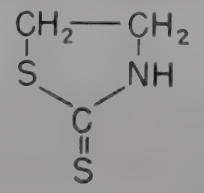
(Bottom Left)

5-(p-DIMETHYLAMINOBENZAL) RHODANINE



(Bottom Center)

2-THIOTHIAZOLIDONE



(Bottom Right)

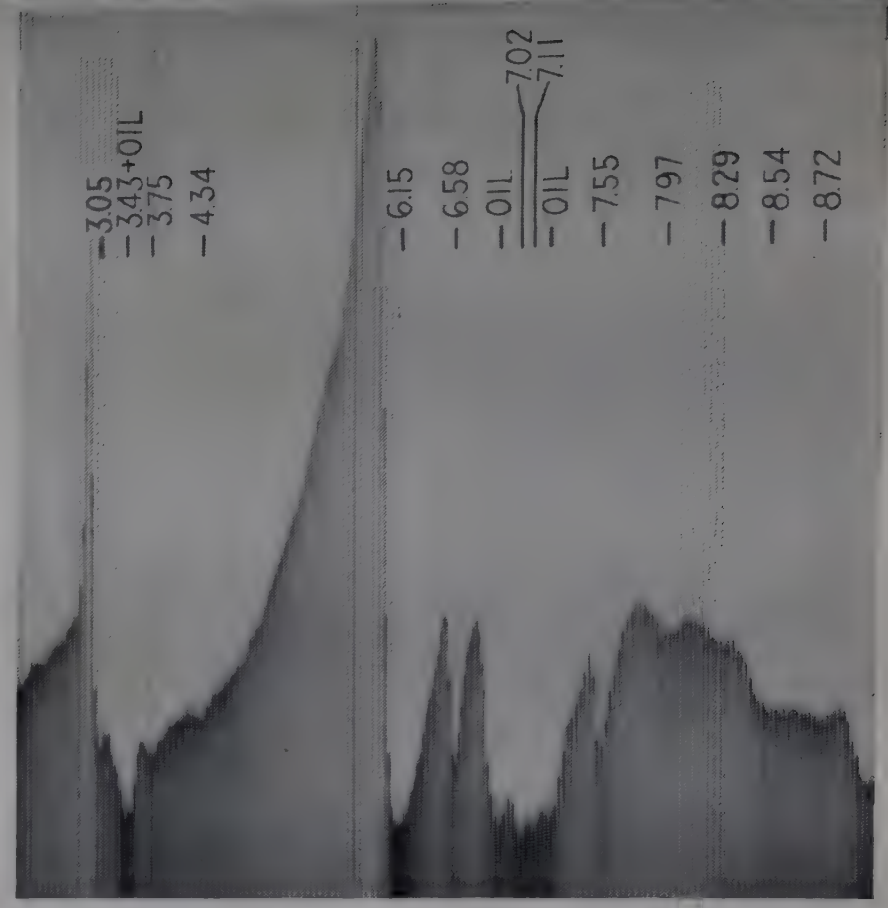


PLATE 241. Assignments: Preparations: Oil paste

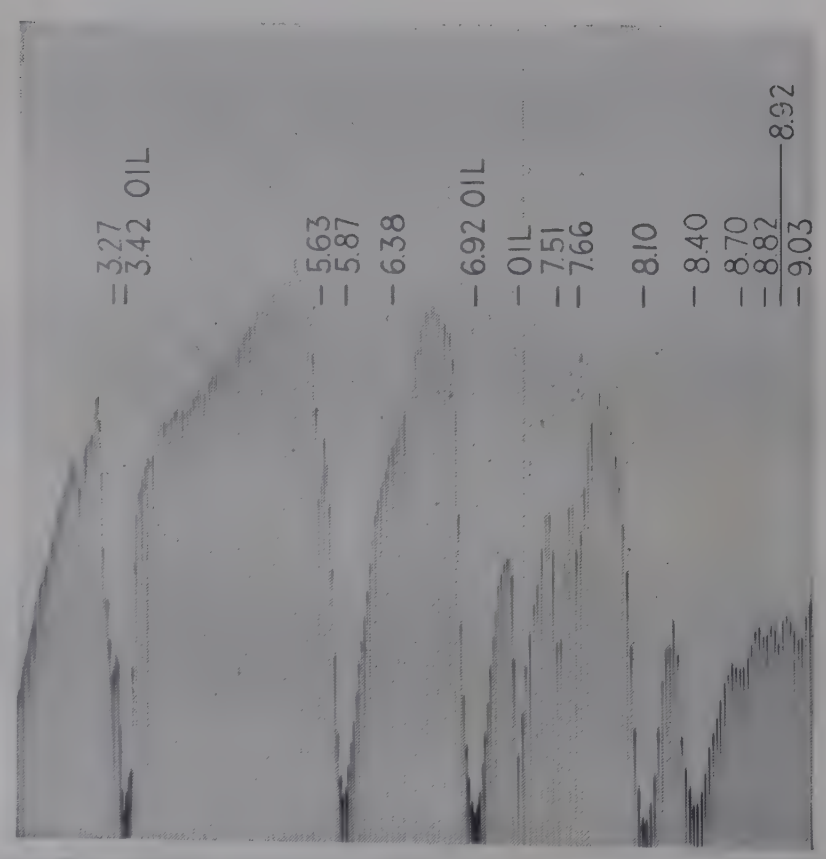


PLATE 242. Assignments: 5.87 μ 4-C=O
6.92 μ Thioureide ion
Preparations: Oil paste

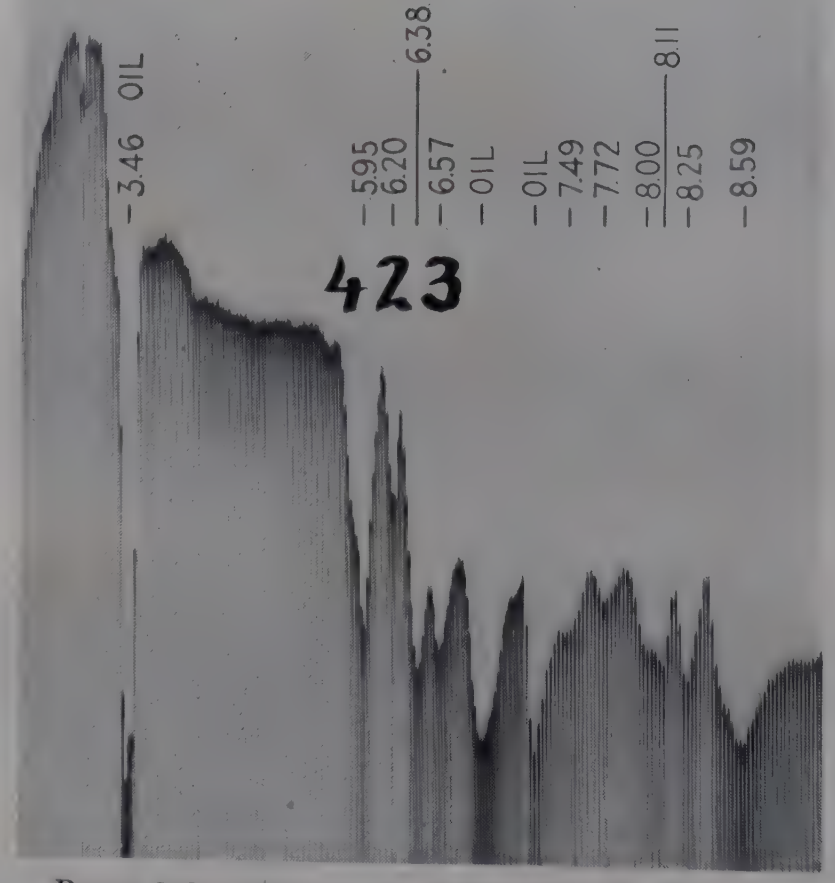


PLATE 243. Assignments: 5.95 μ 4-C=O
6.20 μ Phenyl
6.38 μ Thioureide ion
6.57 μ Anilino
Preparations: Oil paste

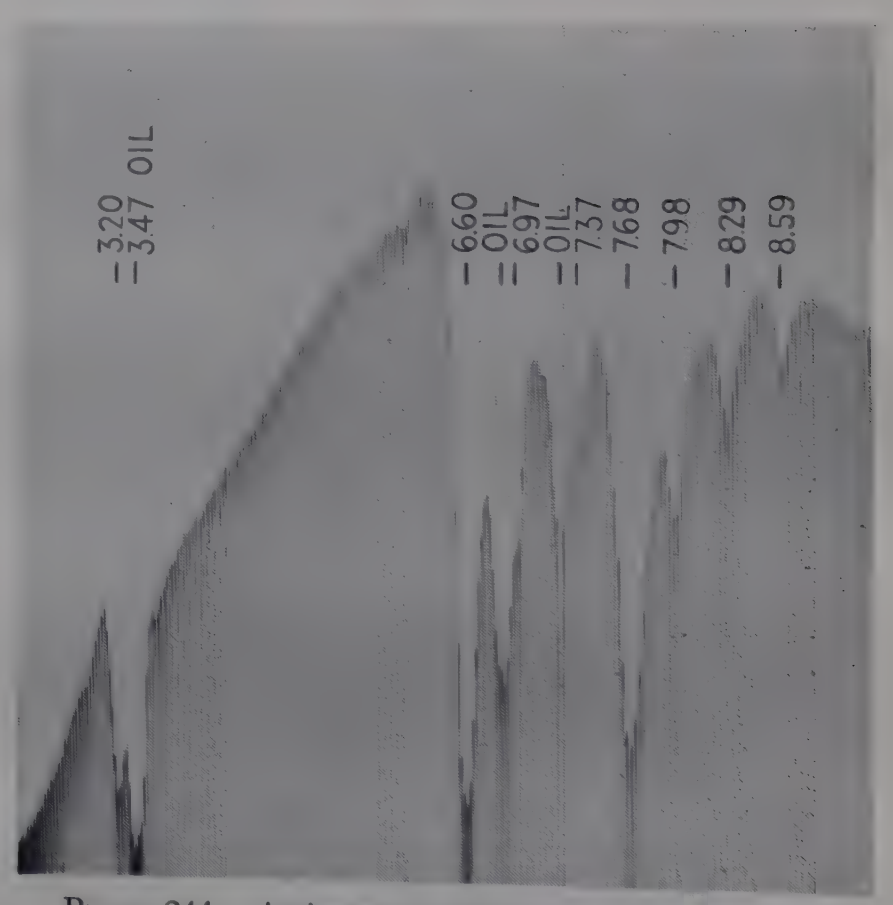
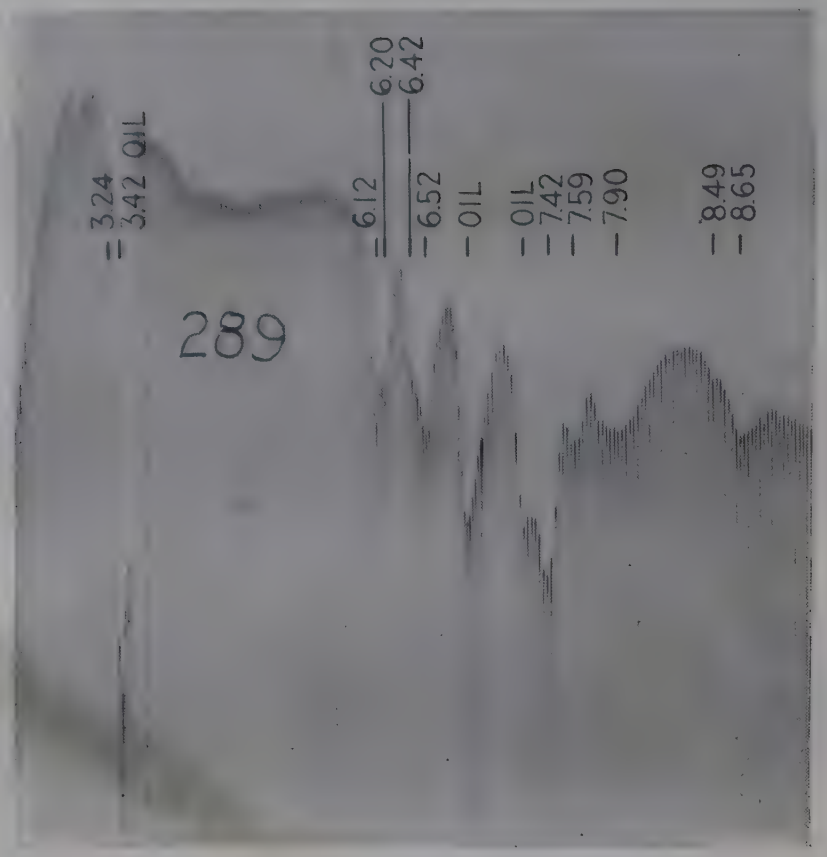
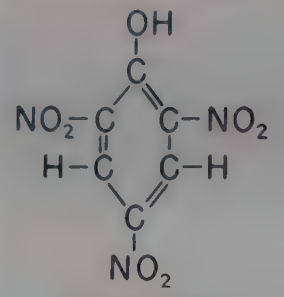


PLATE 244. Assignments: 6.60 μ Thioureide ion
Preparations: Oil paste

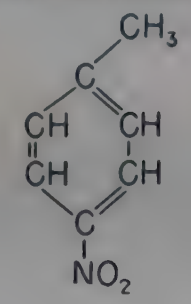


PICRIC ACID

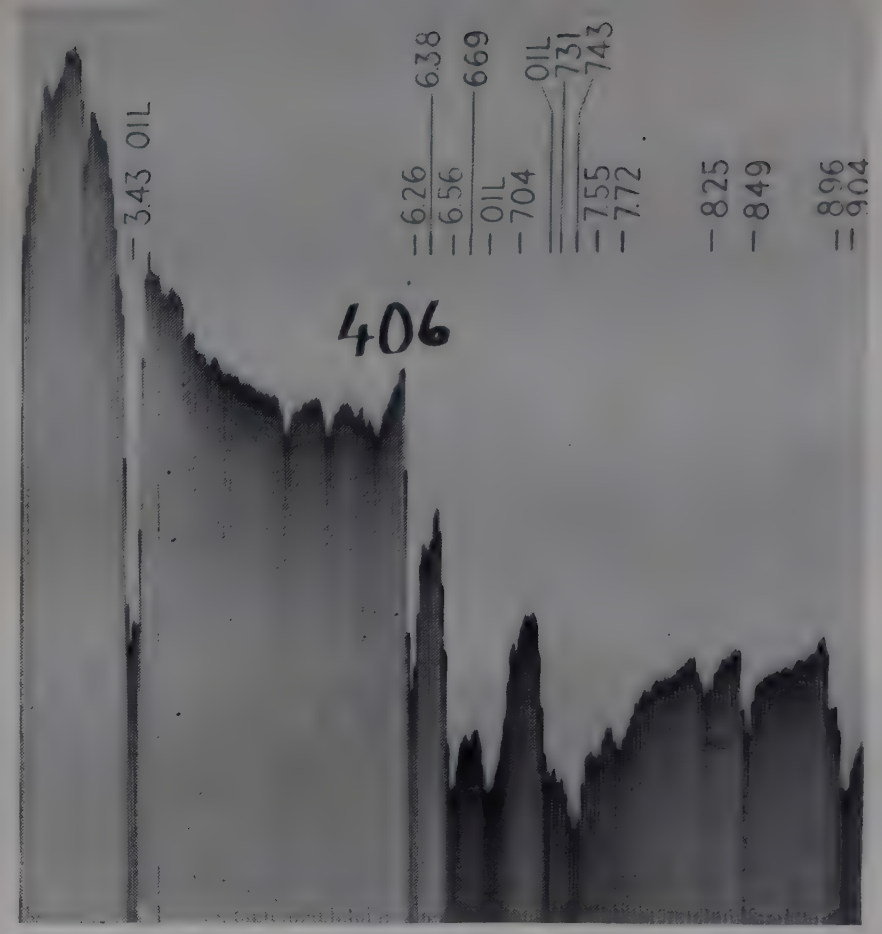


(Top Left)

p-NITROTOLUENE



(Top Right)



NITROMETHANE

CH_3-NO_2

(Bottom)

PLATE 245. Preparations: Oil paste

PLATE 246. Assignments: 6.56 μ NO_2
Preparations: Oil paste

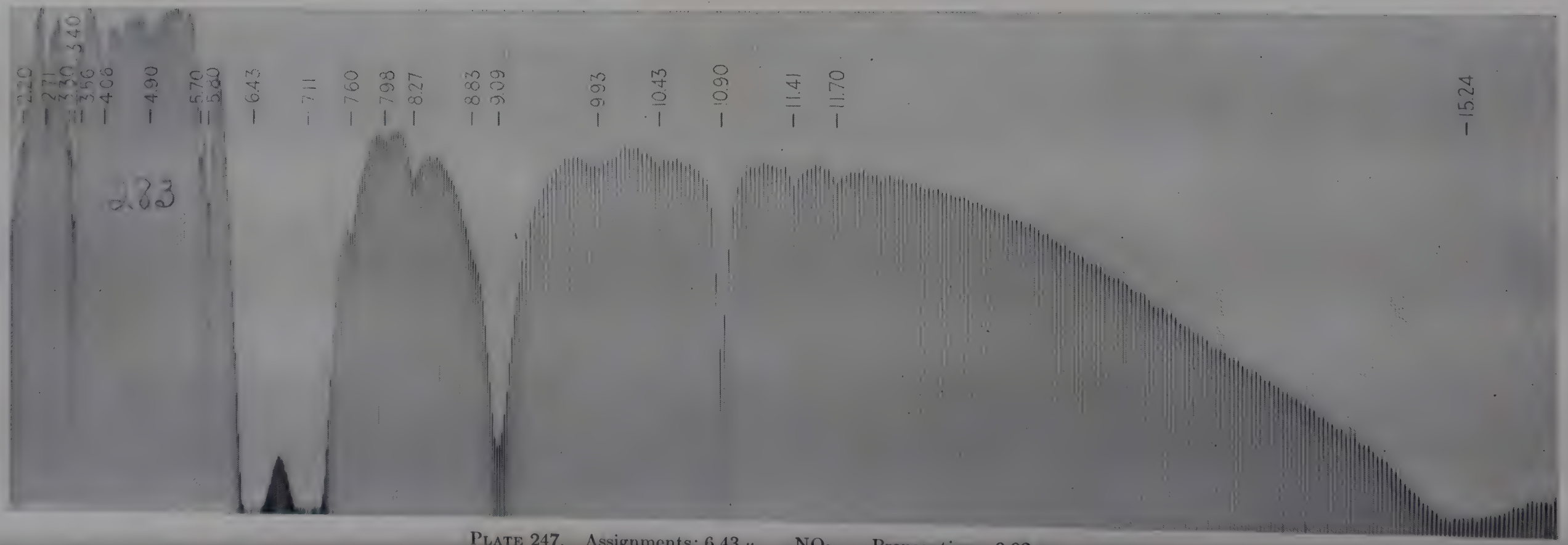


PLATE 247. Assignments: 6.43 μ NO_2 Preparations: 0.02 mm.

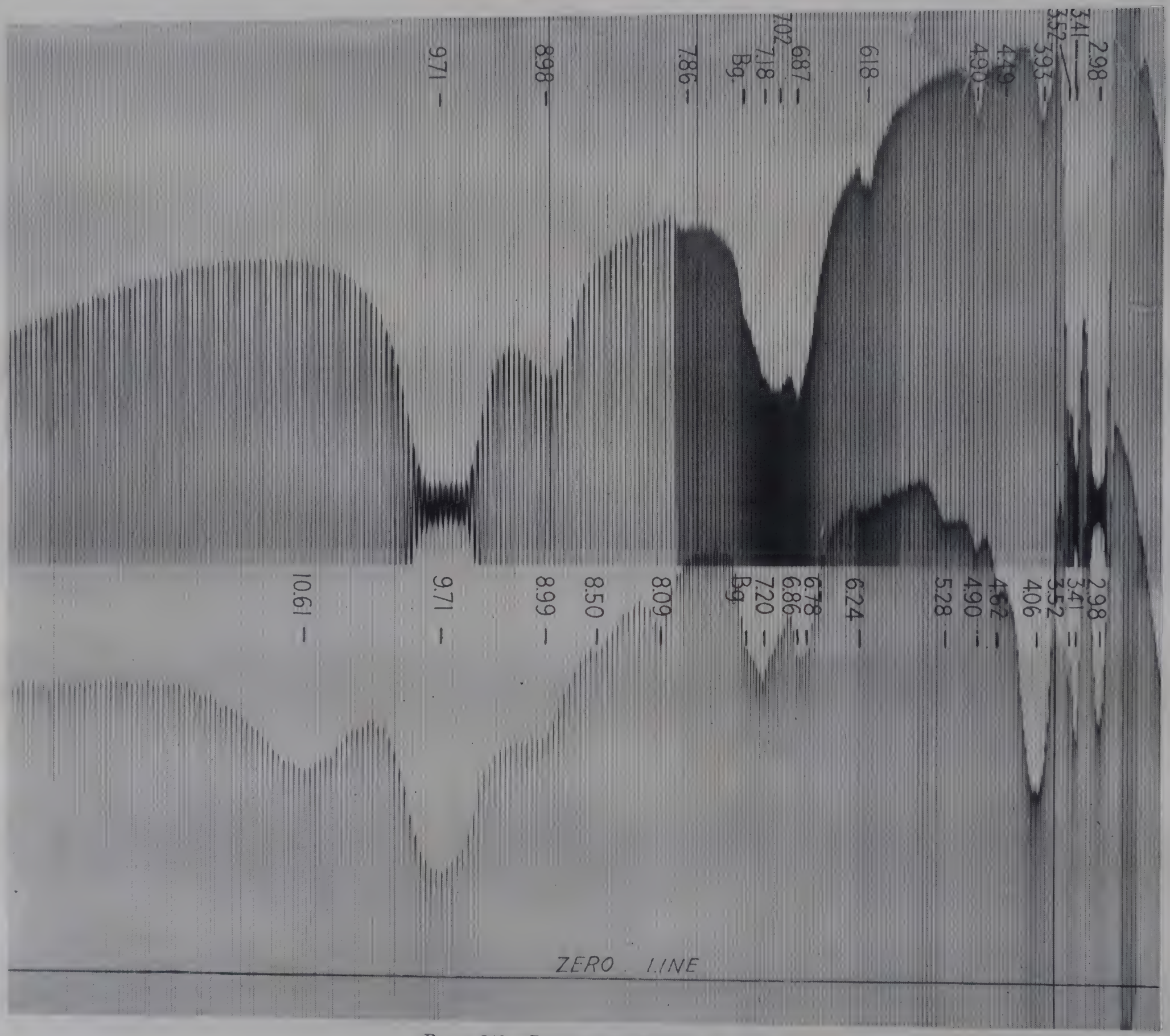


PLATE 248. Preparations: 0.015 mm. (*Top*)
PLATE 249. Preparations: 0.015 mm. (*Bottom*)

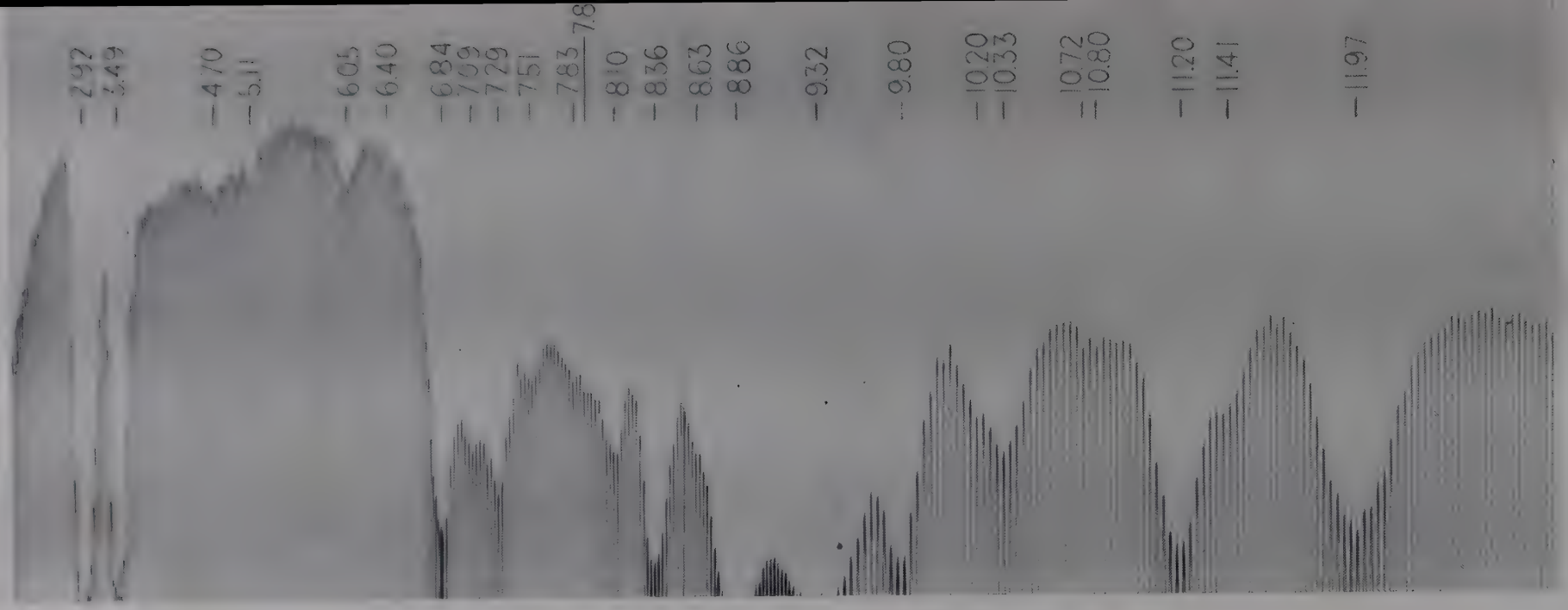


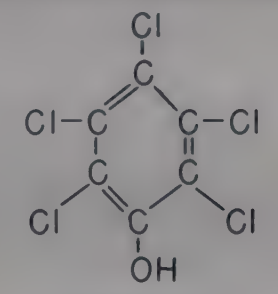
PLATE 252. Preparations: 0.015 mm.

(METHYL CELLOSOLVE)

$CH_3-O-CH_2-CH_2-OH$

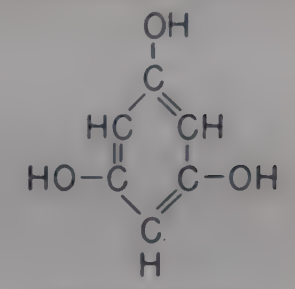
(Top)

PENTACHLOROPHENOL



(Bottom Left)

TRIHYDROXYBENZENE
(SYMMETRICAL)



(Bottom Right)

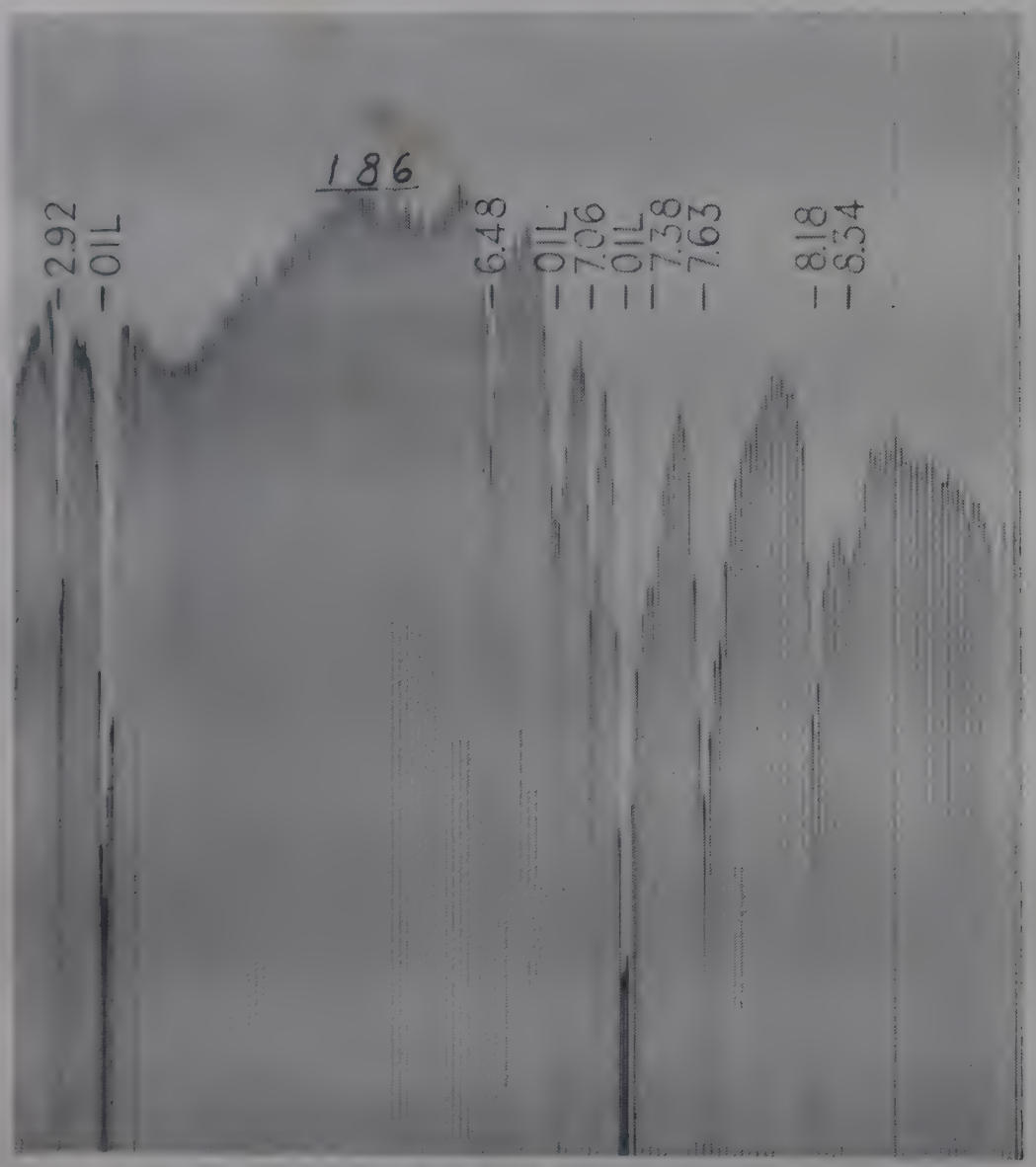


PLATE 250. Assignments: 6.48 μ Ring Preparations: Oil paste

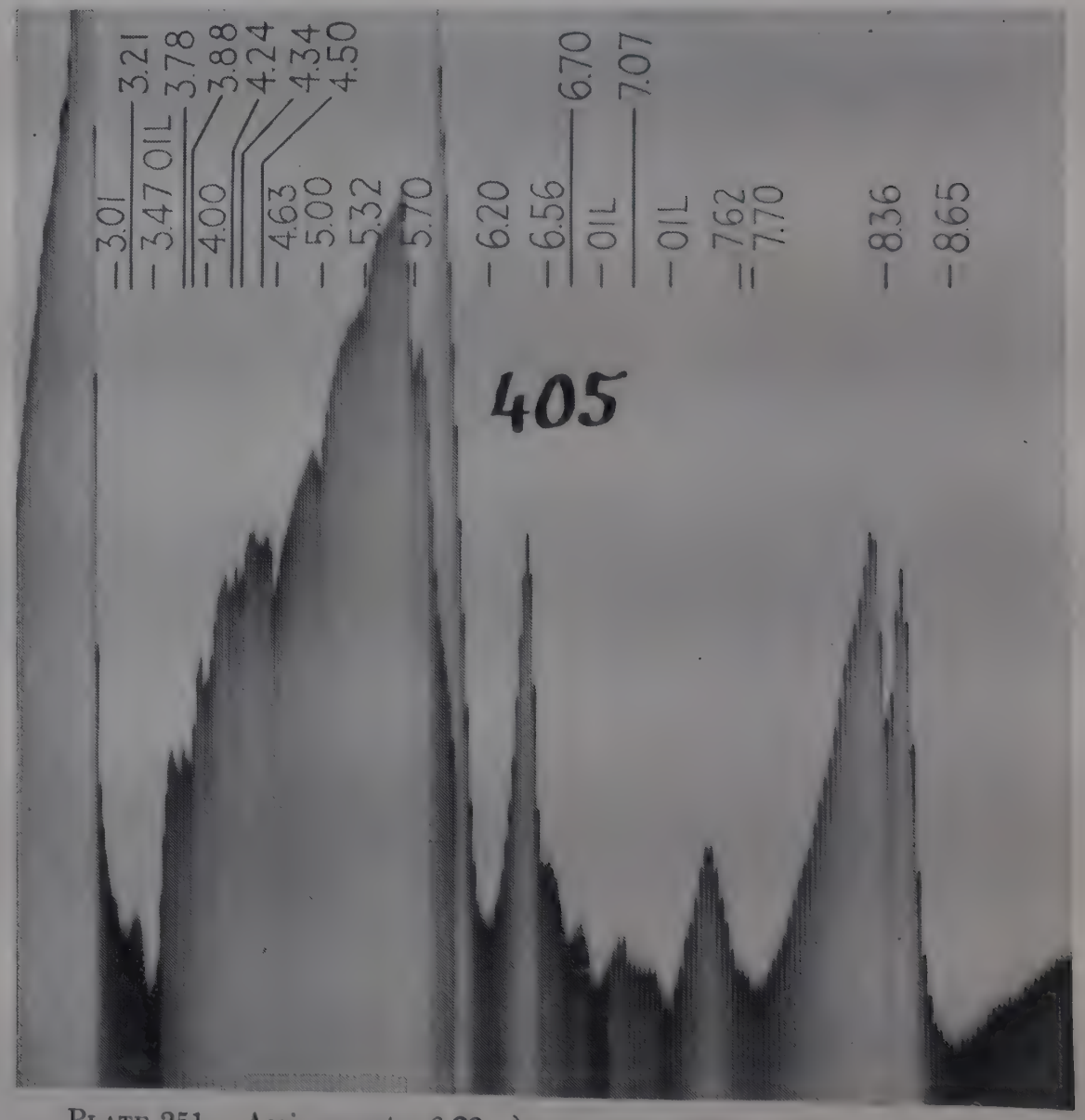
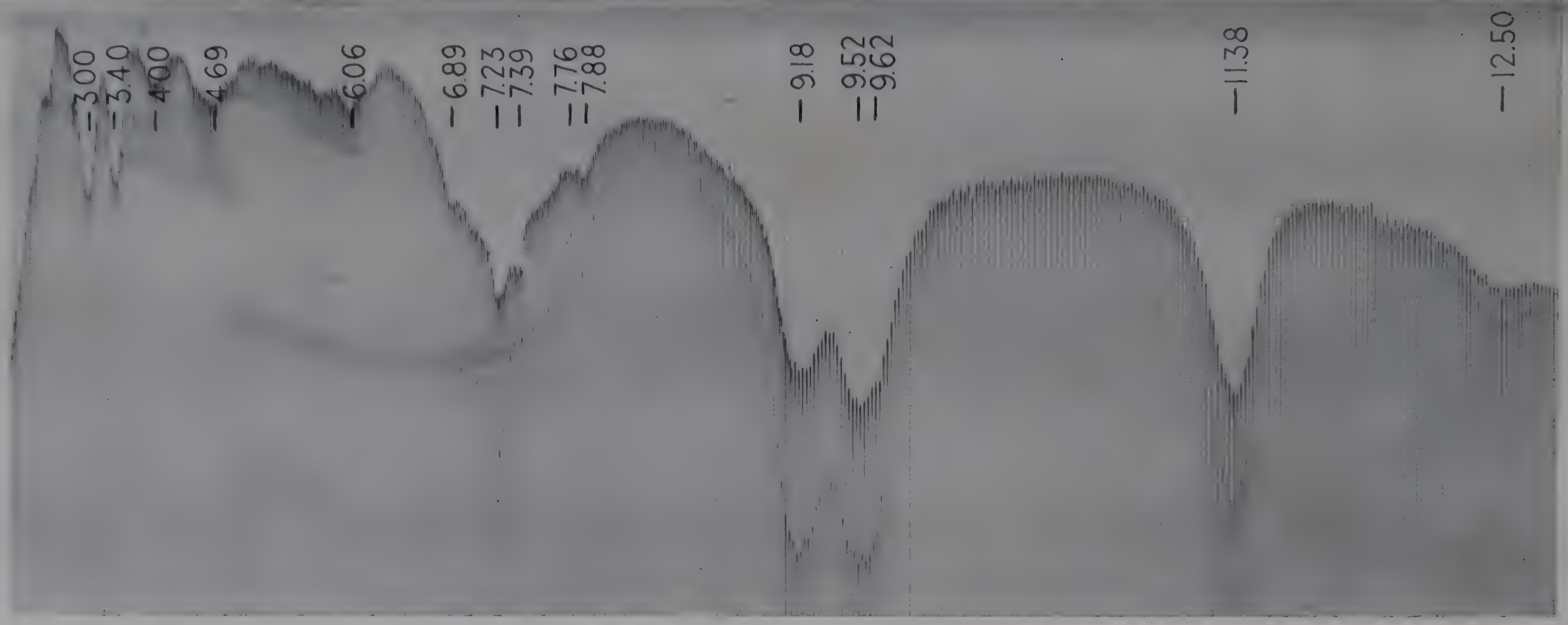


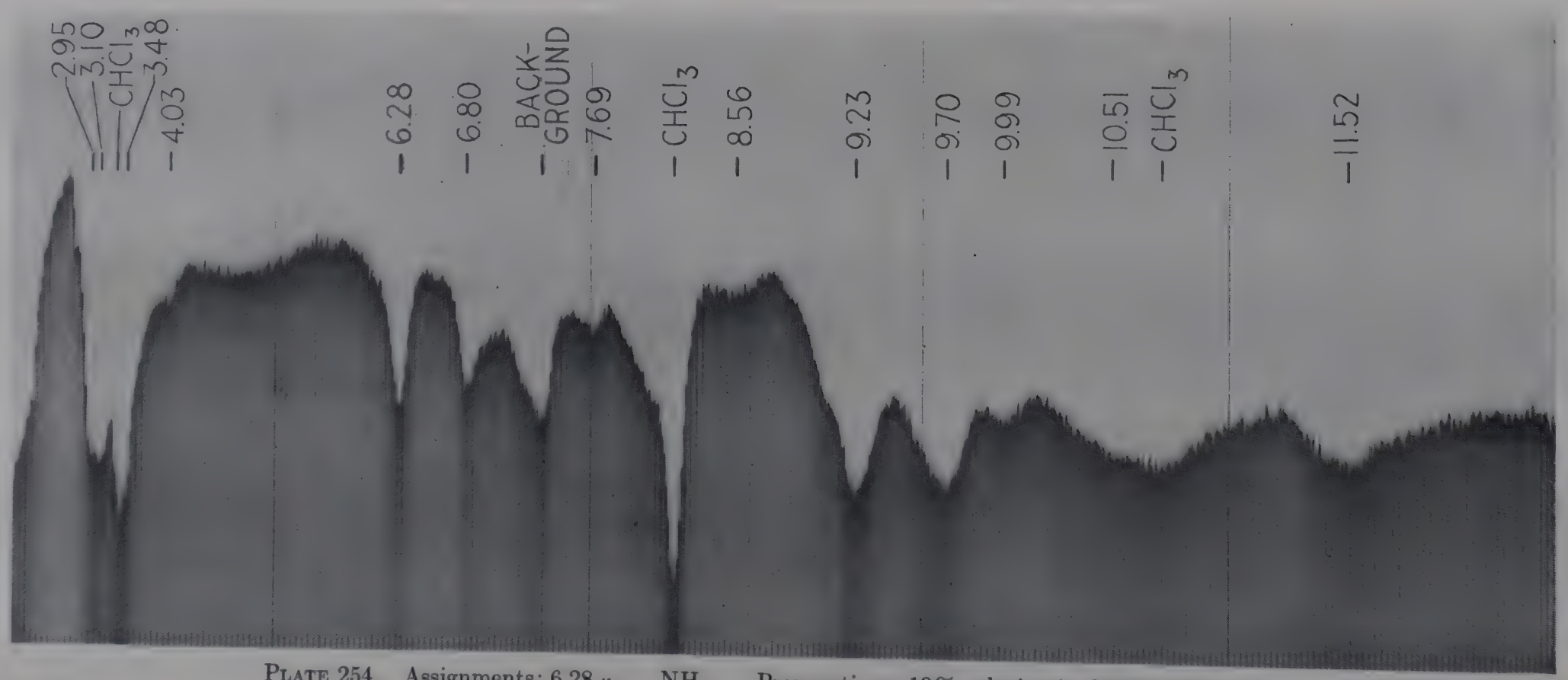
PLATE 251. Assignments: 6.20 μ, 6.56 μ, 6.70 μ Ring Preparations: Oil paste



ETHANOL

C_2H_5-OH

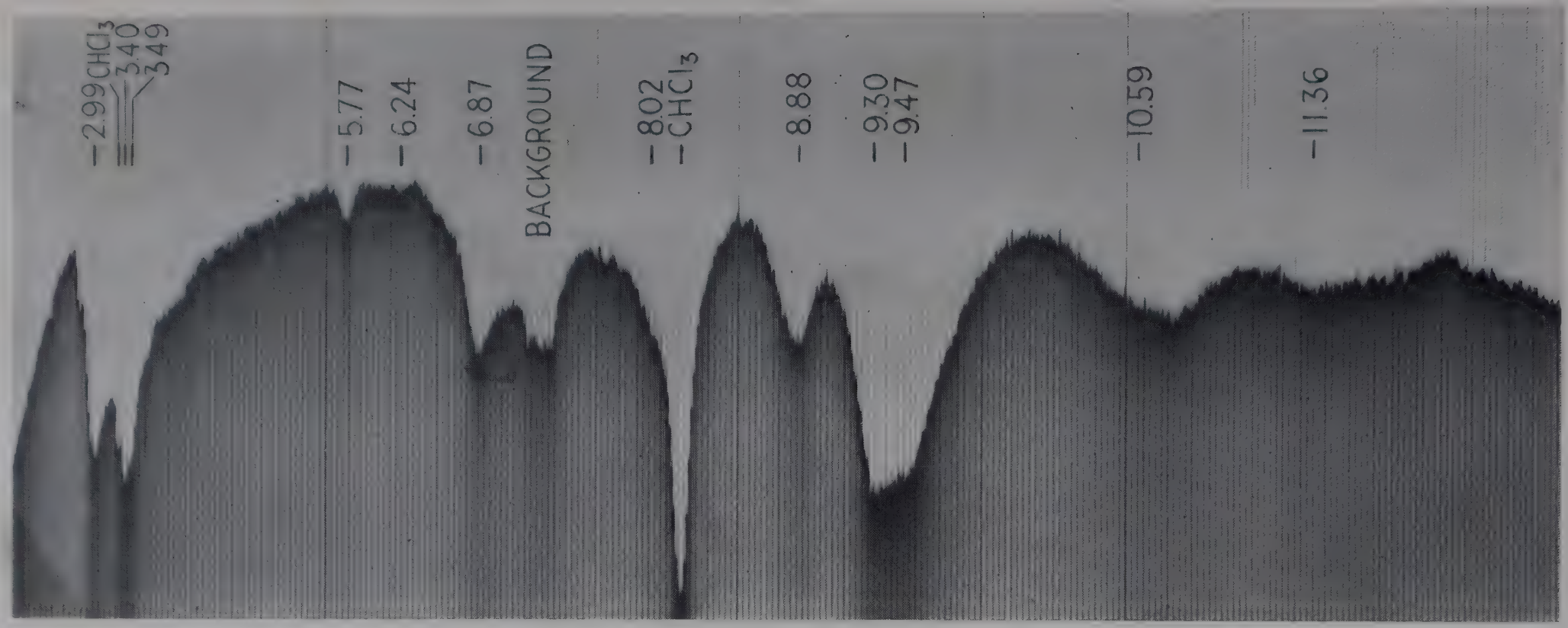
PLATE 253. Preparations: 0.015 mm.



ETHANOLAMINE

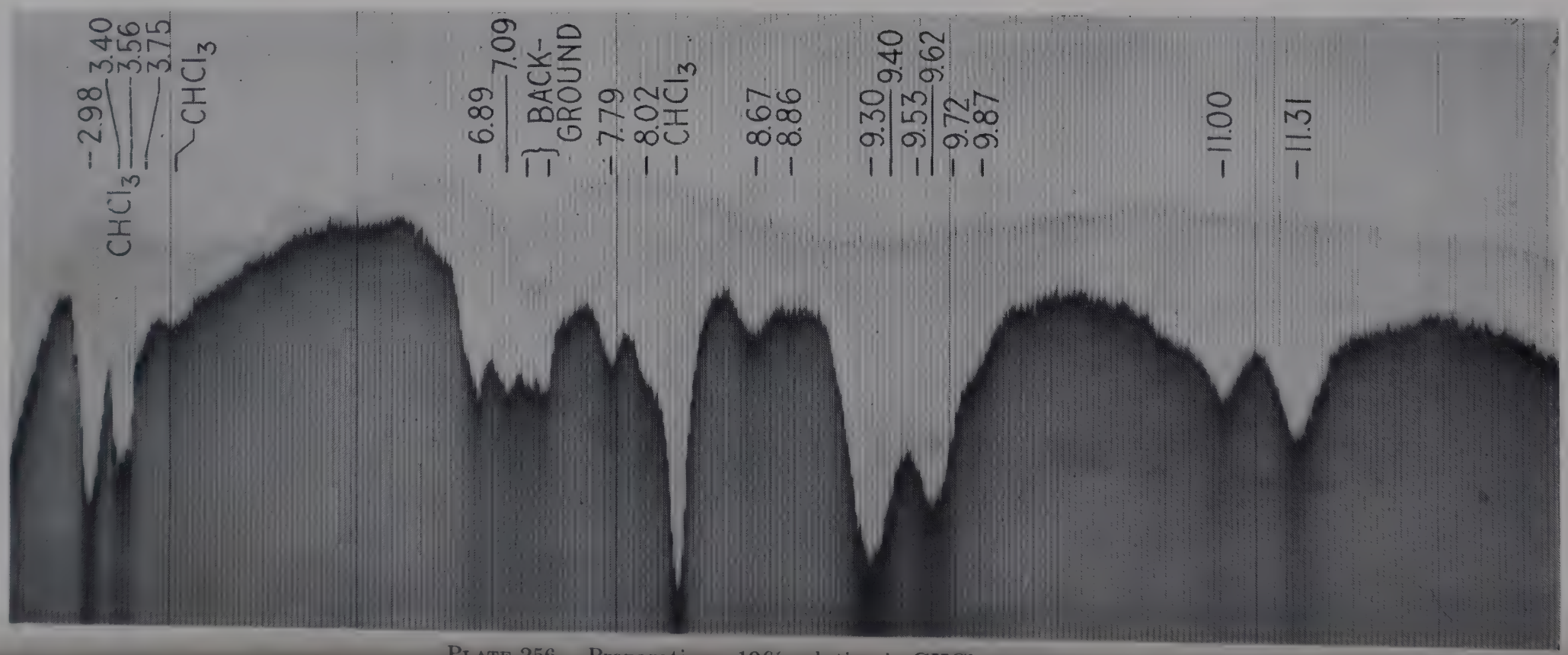
$HO-CH_2-CH_2-NH_2$

PLATE 254. Assignments: 6.28 μ NH_2 Preparations: 10% solution in $CHCl_3$, 0.015 mm.



DIETHANOLAMINE
$(HO-CH_2-CH_2)_2-NH$

PLATE 255. Preparations: 10% solution in $CHCl_3$ 0.015 mm.



TRIETHANOLAMINE
$(HOC_2H_4)_3N$

PLATE 256. Preparations: 10% solution in $CHCl_3$, 0.015 mm.

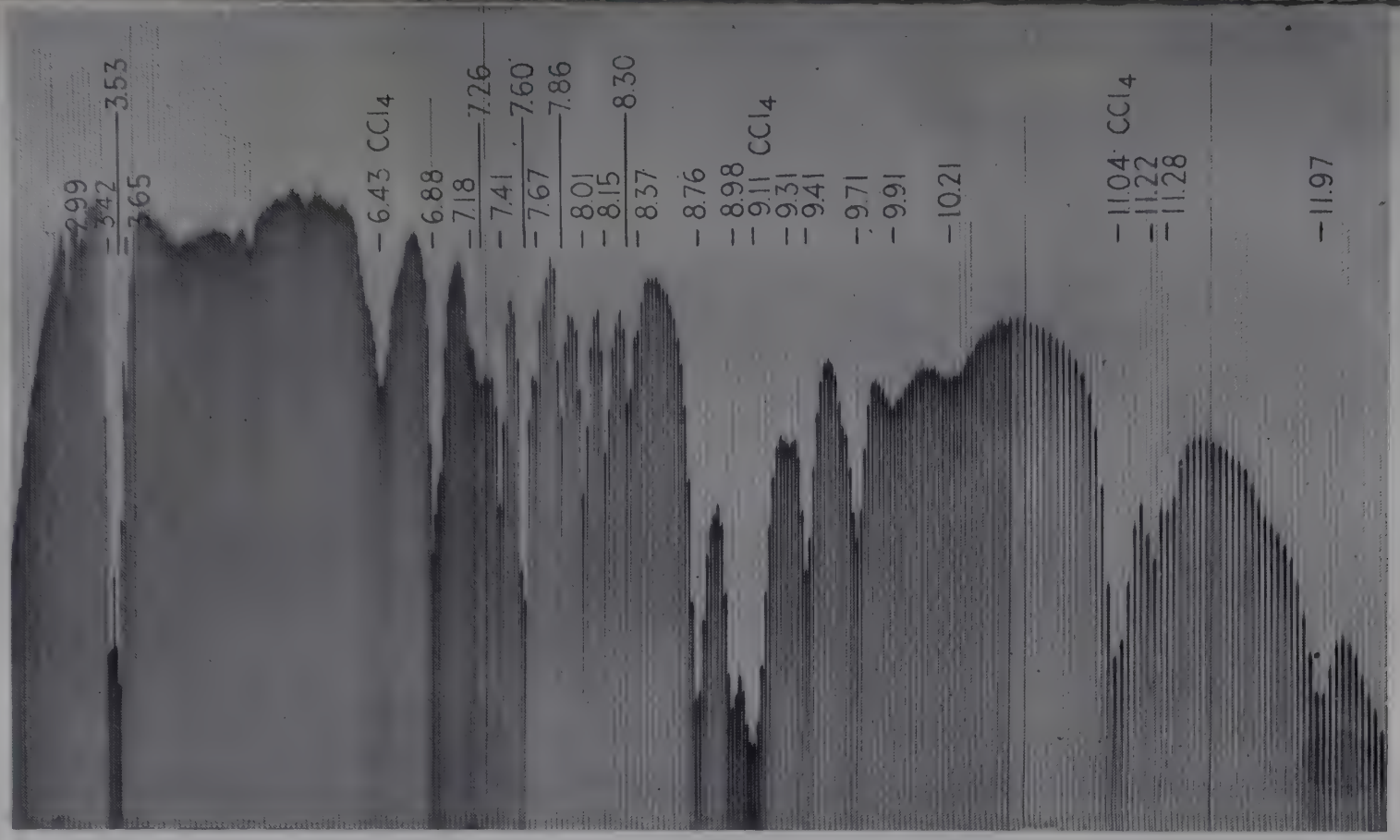
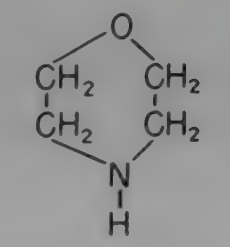


PLATE 258. Preparations: 10% solution in CCl_4, 0.08 mm.

MORPHOLINE



(*Both plates*)

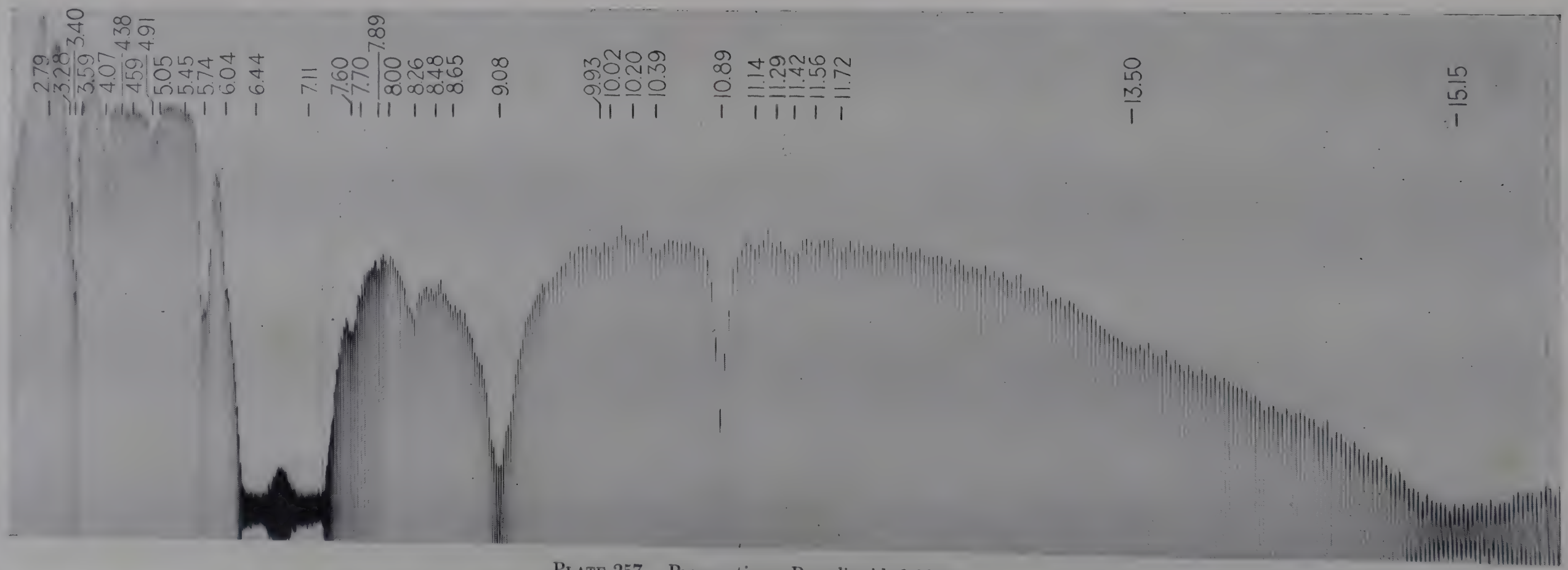
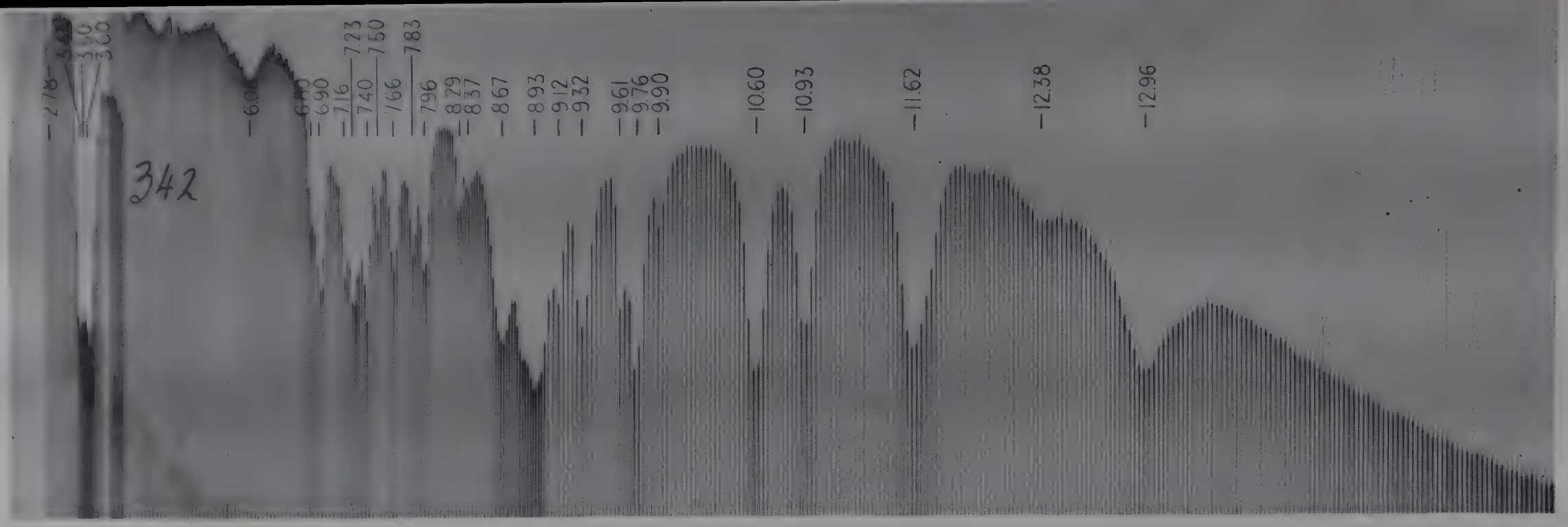


PLATE 257. Preparations: Pure liquid, 0.02 mm.



N-METHYL MORPHOLINE

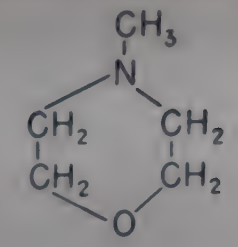
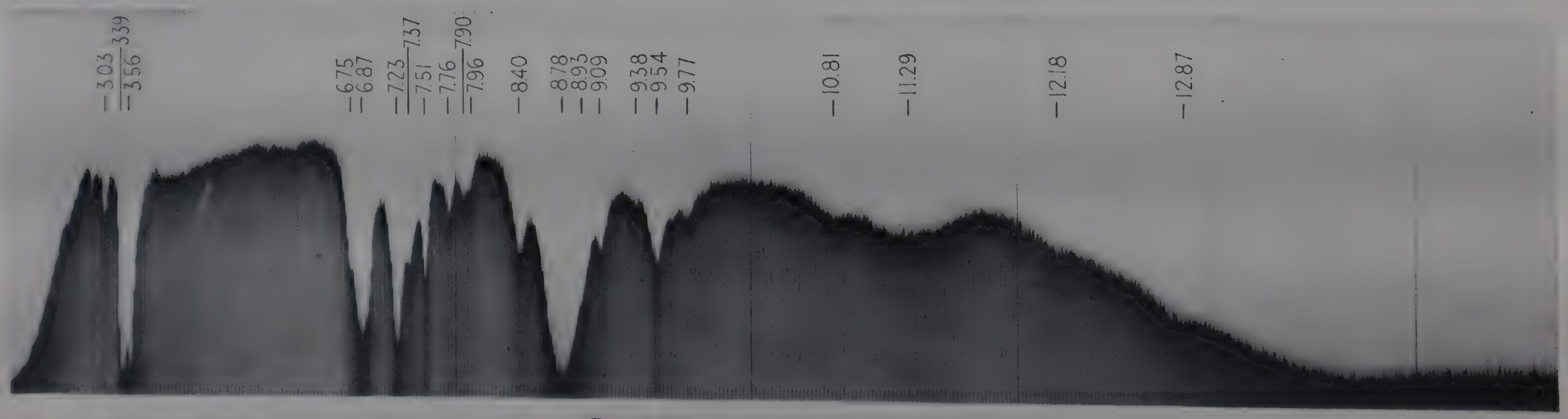


PLATE 259. Preparations: 0.02 mm.



DIETHYLAMINE

$(C_2H_5)_2NH$

PLATE 260. Preparations: 0.015 mm.

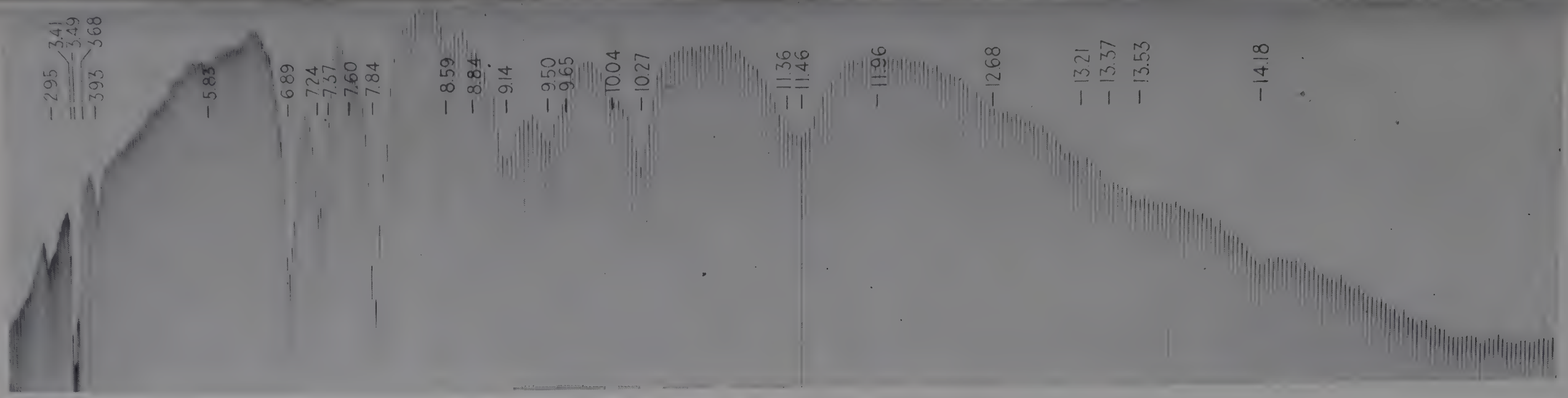
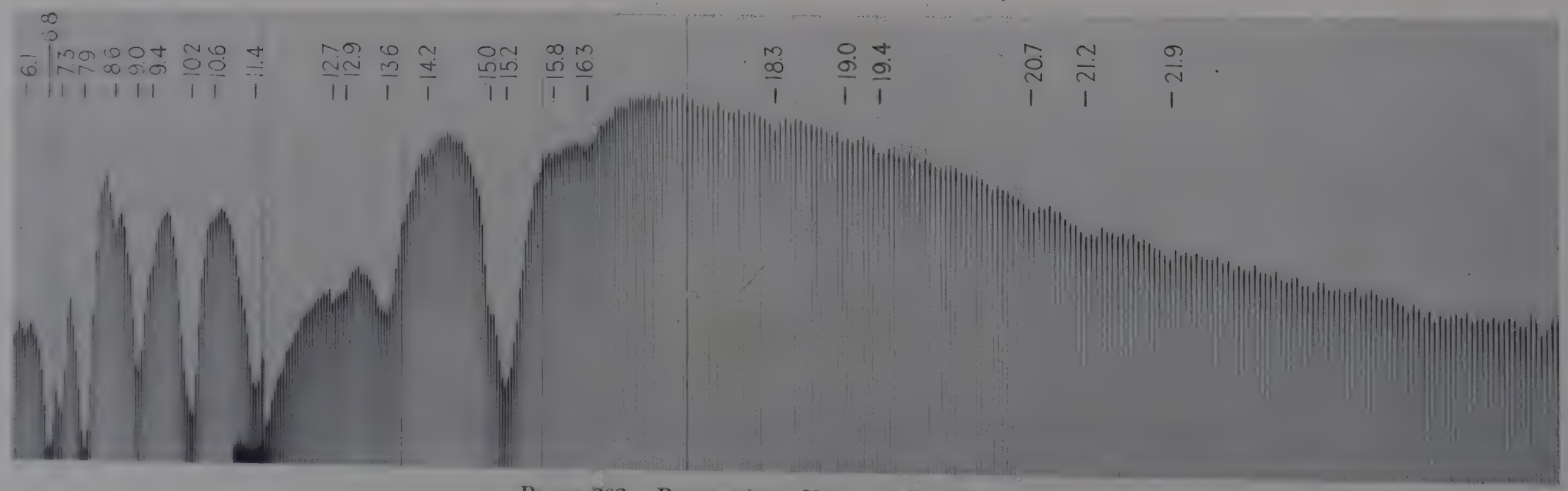


PLATE 261. Preparations: NaCl prism, 0.015 mm.



ETHYL MERCAPTAN
$(C_2H_5)SH$
(Both plates)

PLATE 262. Preparations: KBr prism, 0.08 mm.

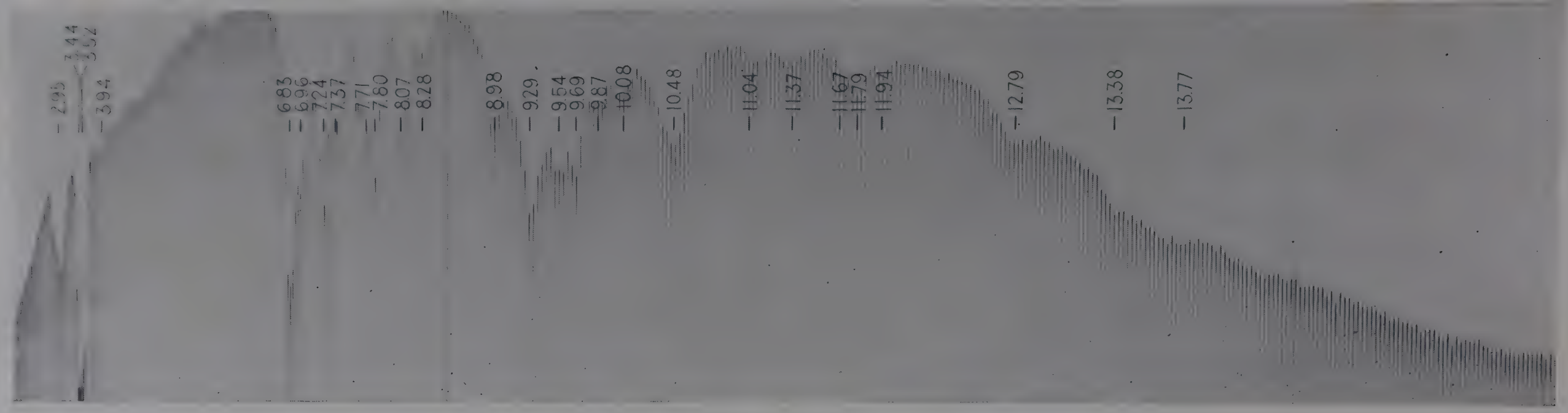
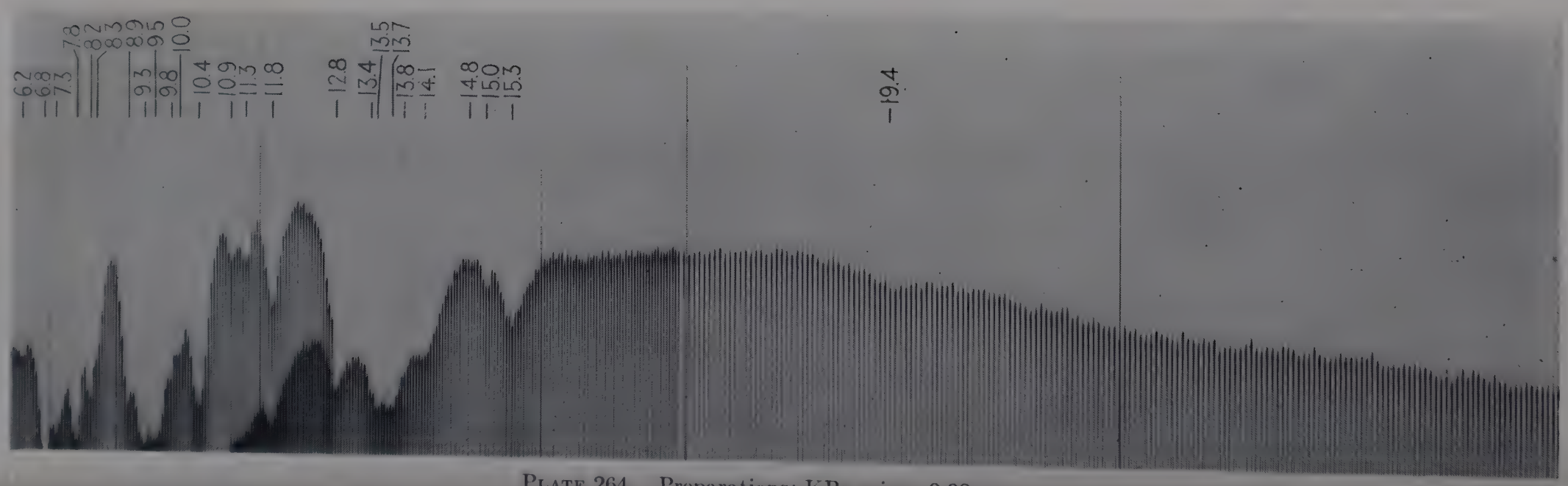


PLATE 263. Preparations: NaCl prism, 0.015 mm.



n-BUTYL MERCAPTAN

$CH_3-(CH_2)_3-SH$

(Both plates)

PLATE 264. Preparations: KBr prism, 0.08 mm.

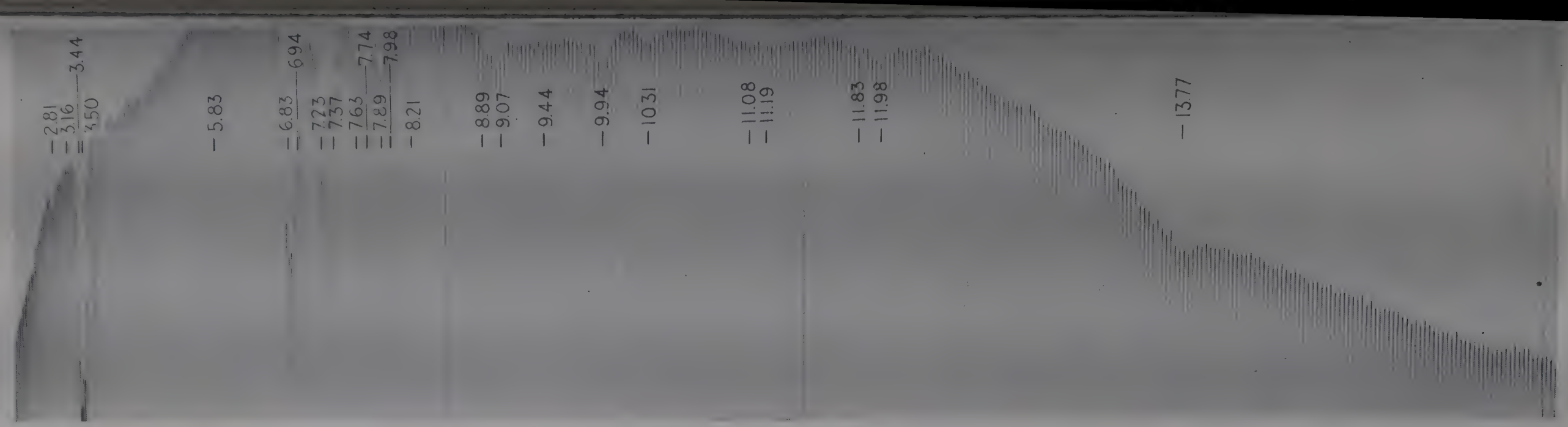
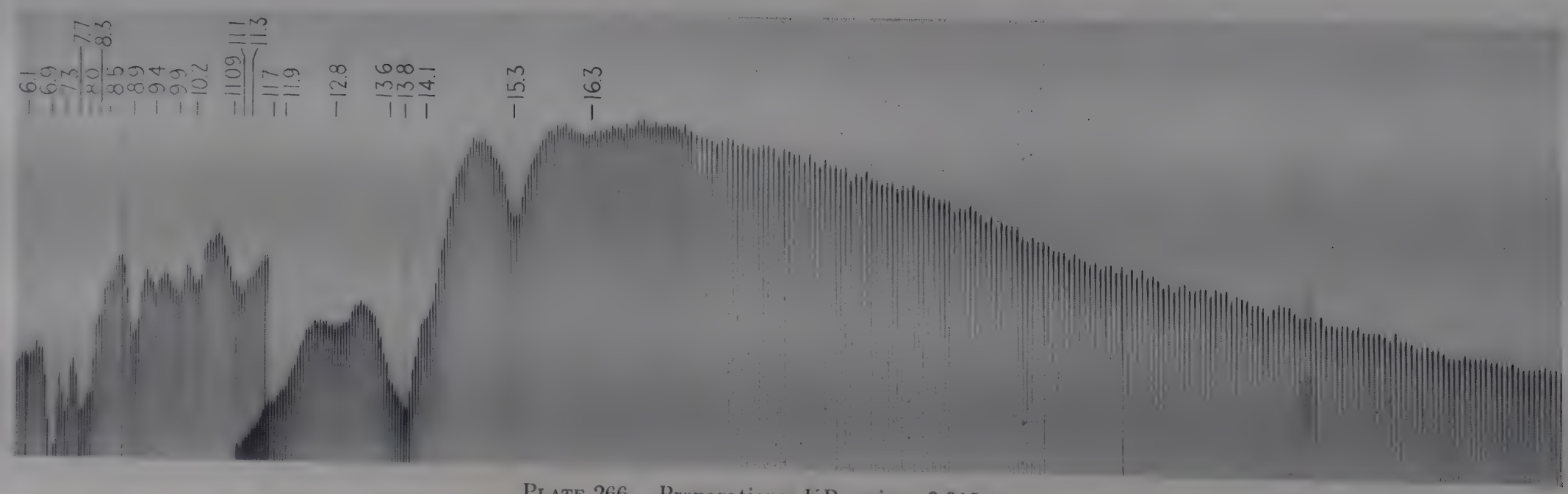


PLATE 265. Preparations: 0.08 mm.



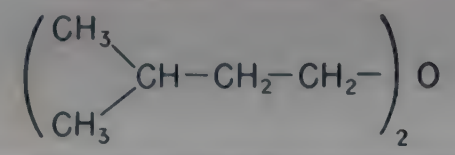
n-HEXYL MERCAPTAN

$CH_3-(CH_2)_5-SH$

(Both plates)

PLATE 266. Preparations: KBr prism, 0.015 mm.

DIISOAMYL ETHER



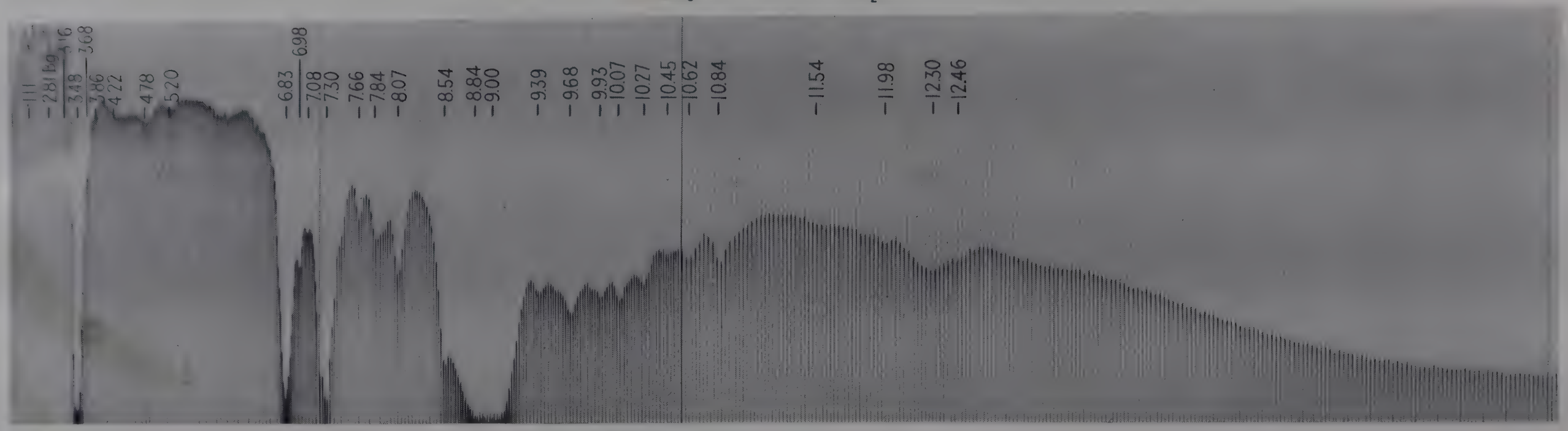


PLATE 267. Preparations: 0.015 mm.

ETHYL n-BUTYL ETHER

$CH_3\text{-}CH_2\text{-}O\text{-}(CH_2)_3\text{-}CH_3$

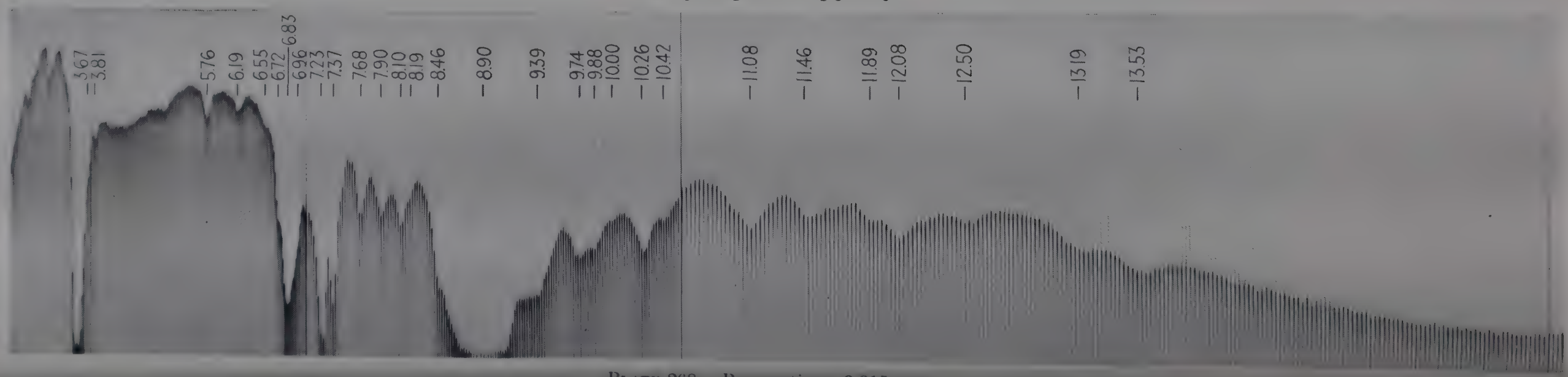
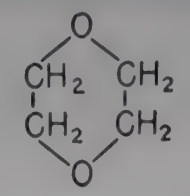


PLATE 268. Preparations: 0.015 mm.

1,4-DIOXANE



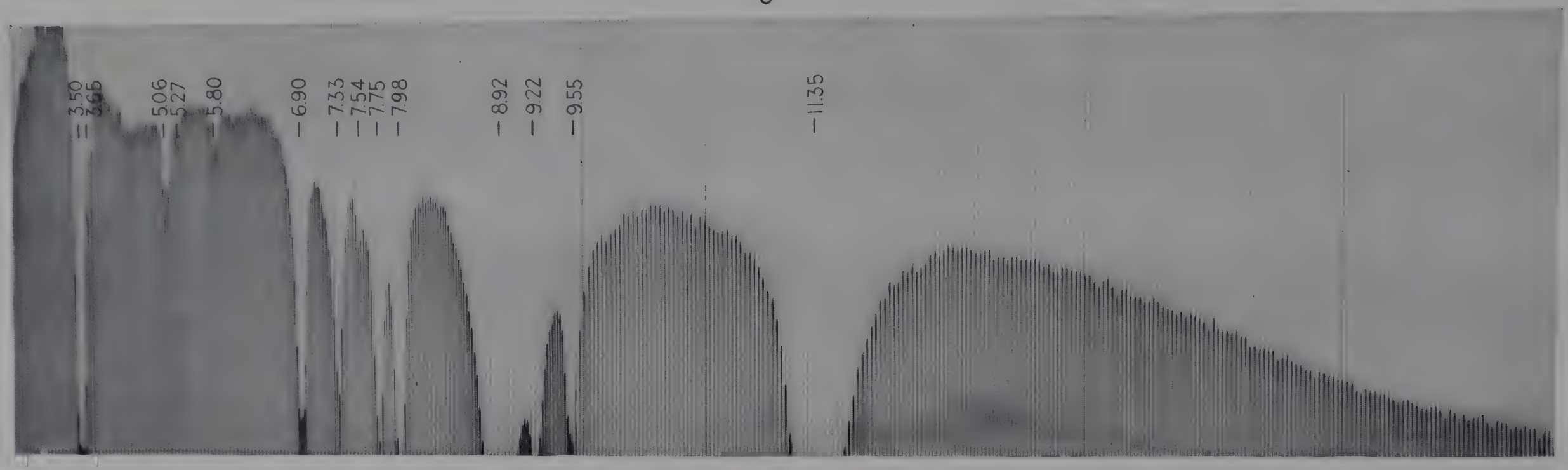


PLATE 269. Preparations: 0.02 mm.

PARAFFIN OIL
(COMMERCIAL MINERAL OIL, NUJOL)

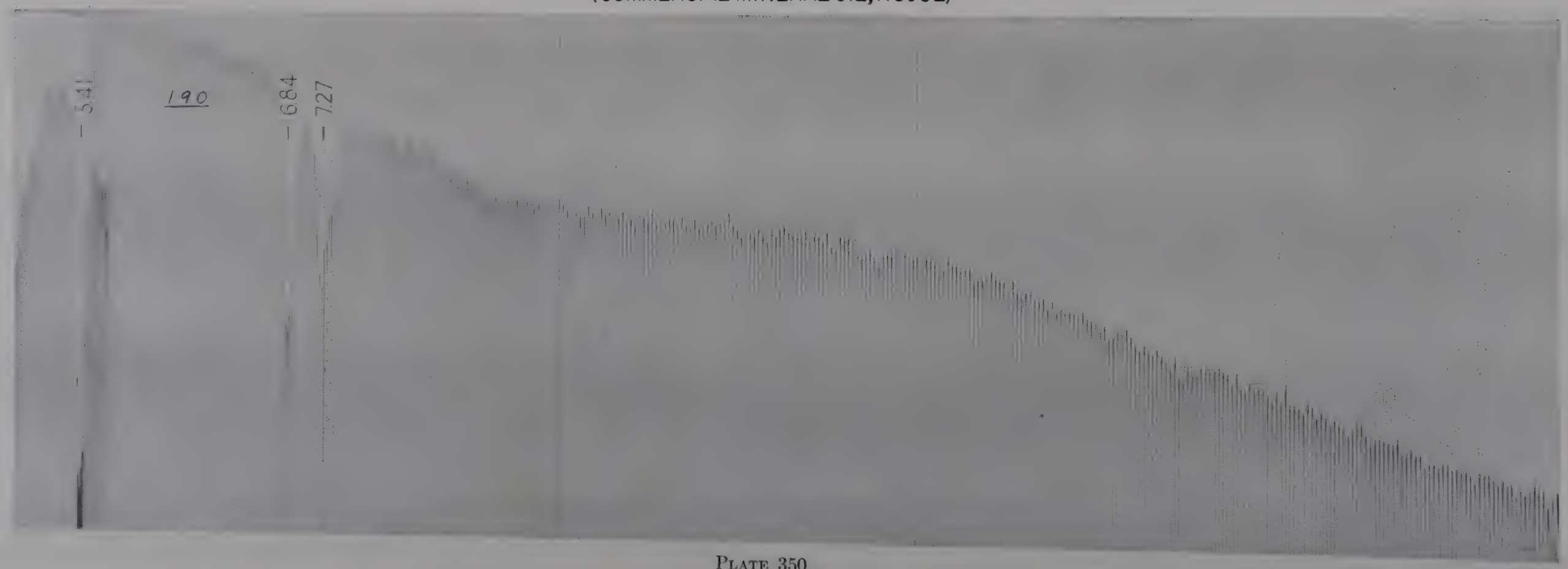


PLATE 350.

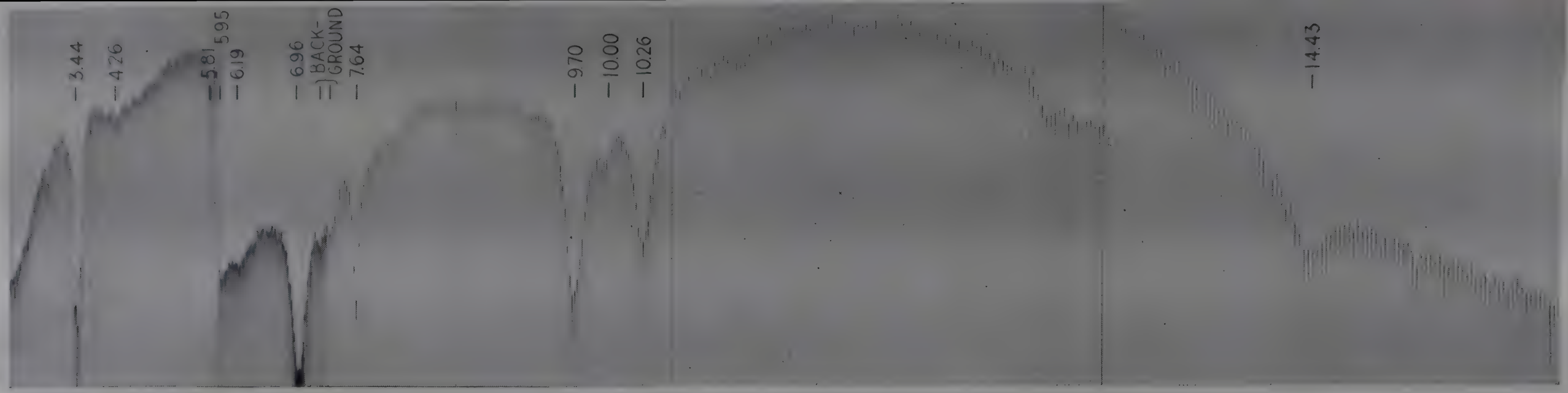
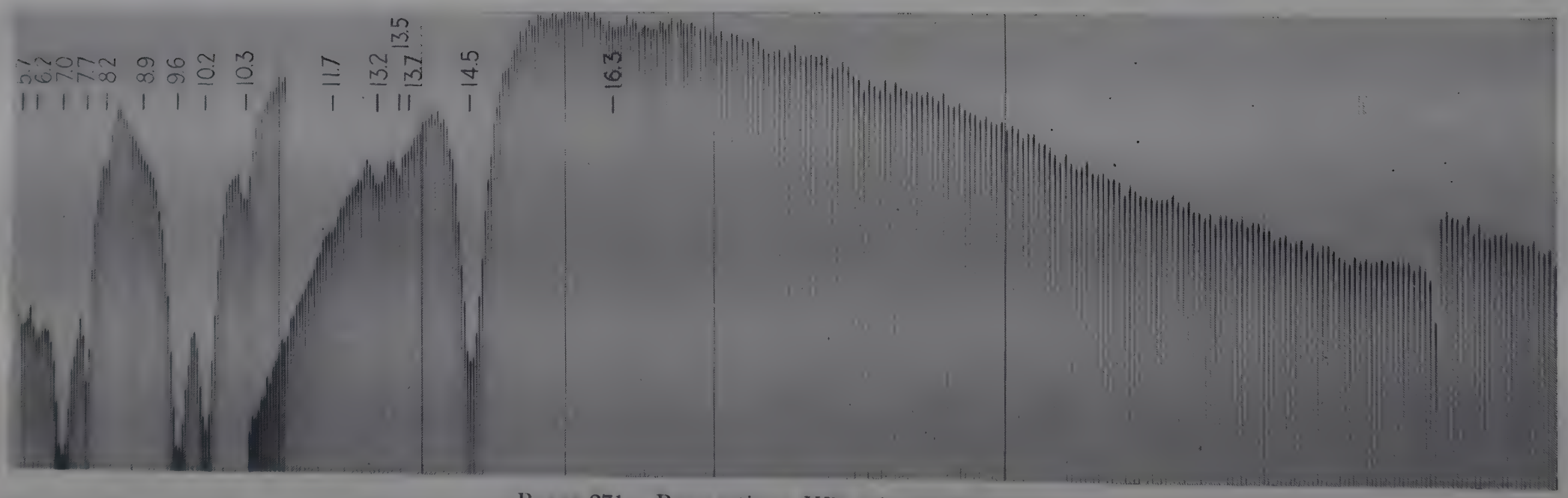


PLATE 270. Preparations: NaCl prism, 0.015



DIMETHYL SULPHIDE

CH_3-S-CH_3

(Both plates)

PLATE 271. Preparations: KBr prism, 0.08 mm.

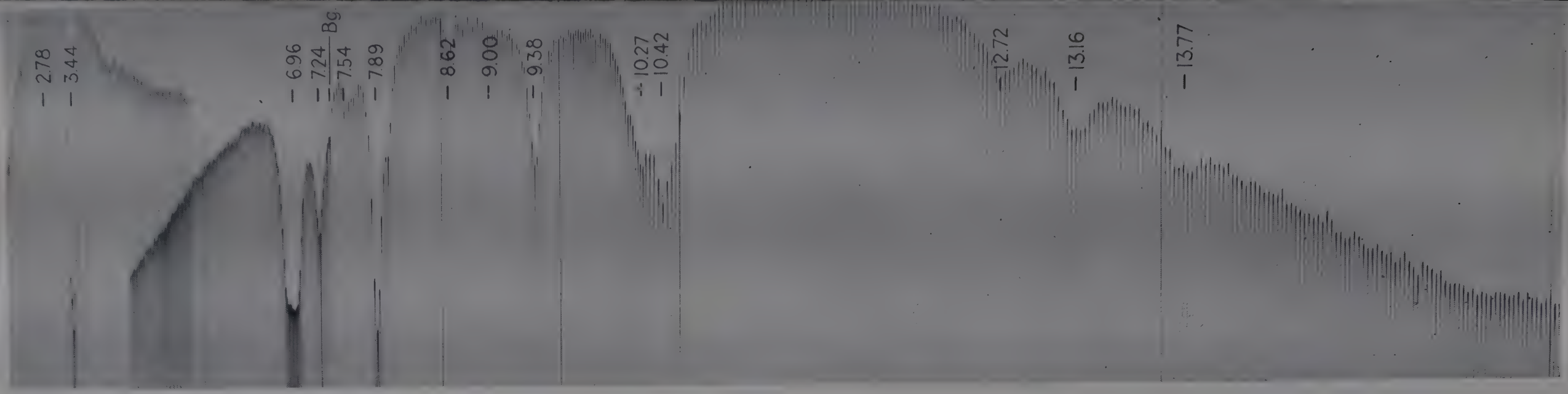
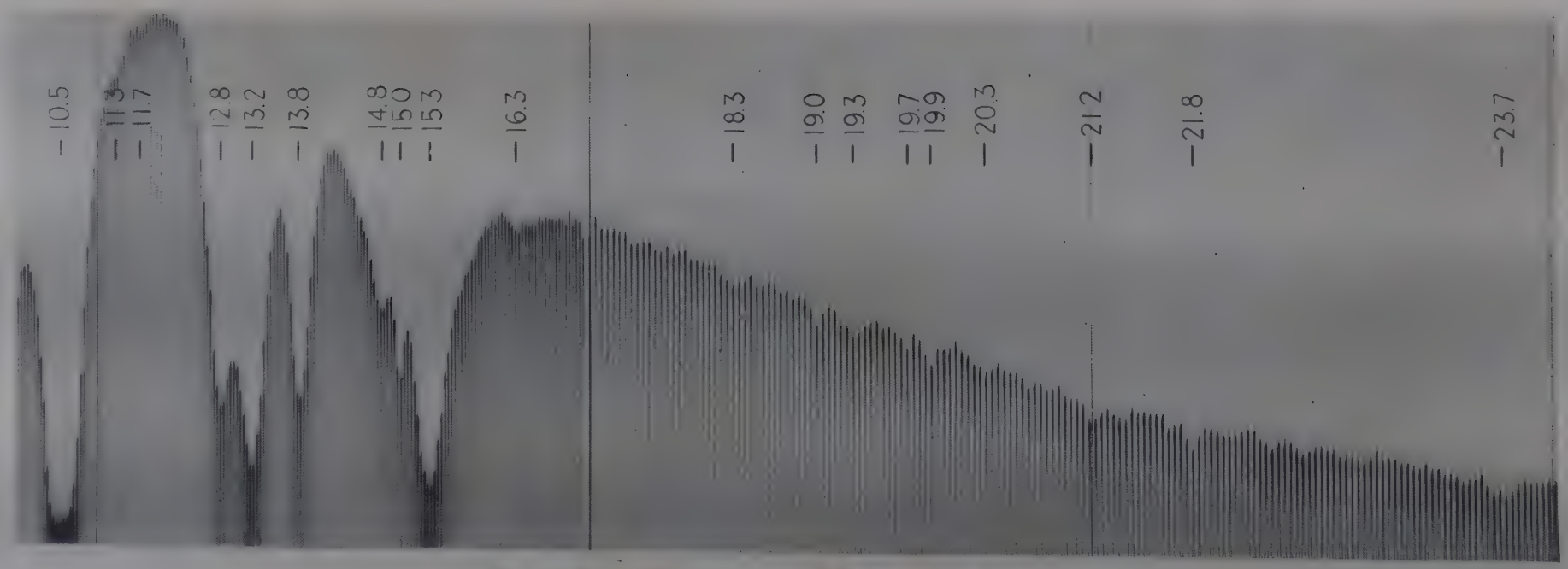


PLATE 272. Preparations: NaCl prism, 0.015 mm.



METHYL ETHYL SULPHIDE

CH_3-S-C_2H_5

(Both plates)

PLATE 273. Preparations: KBr prism, 0.15 mm.

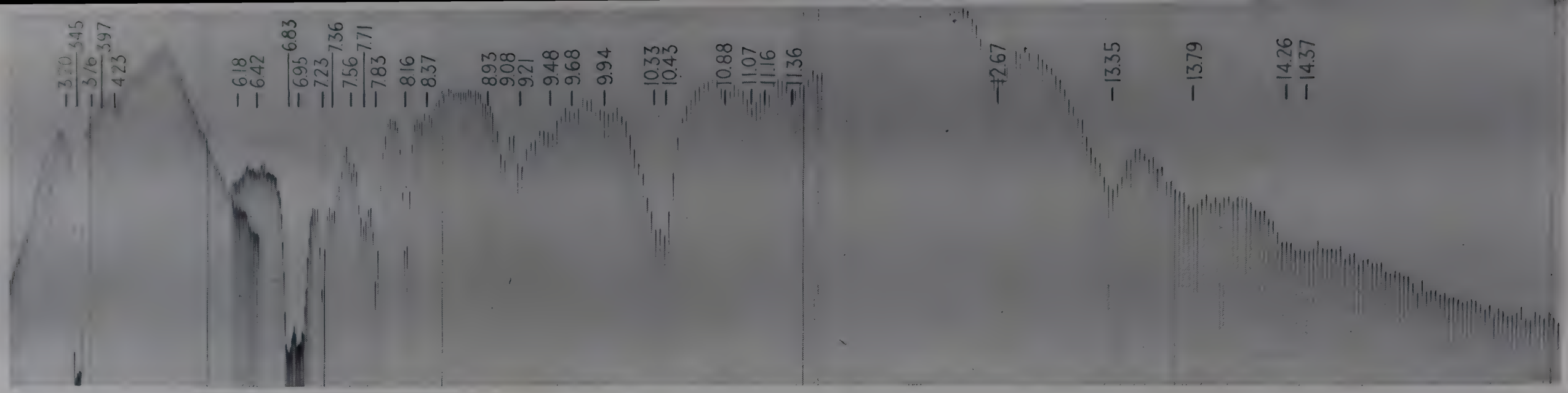


PLATE 274. Preparations: NaCl prism, 0.02 mm.

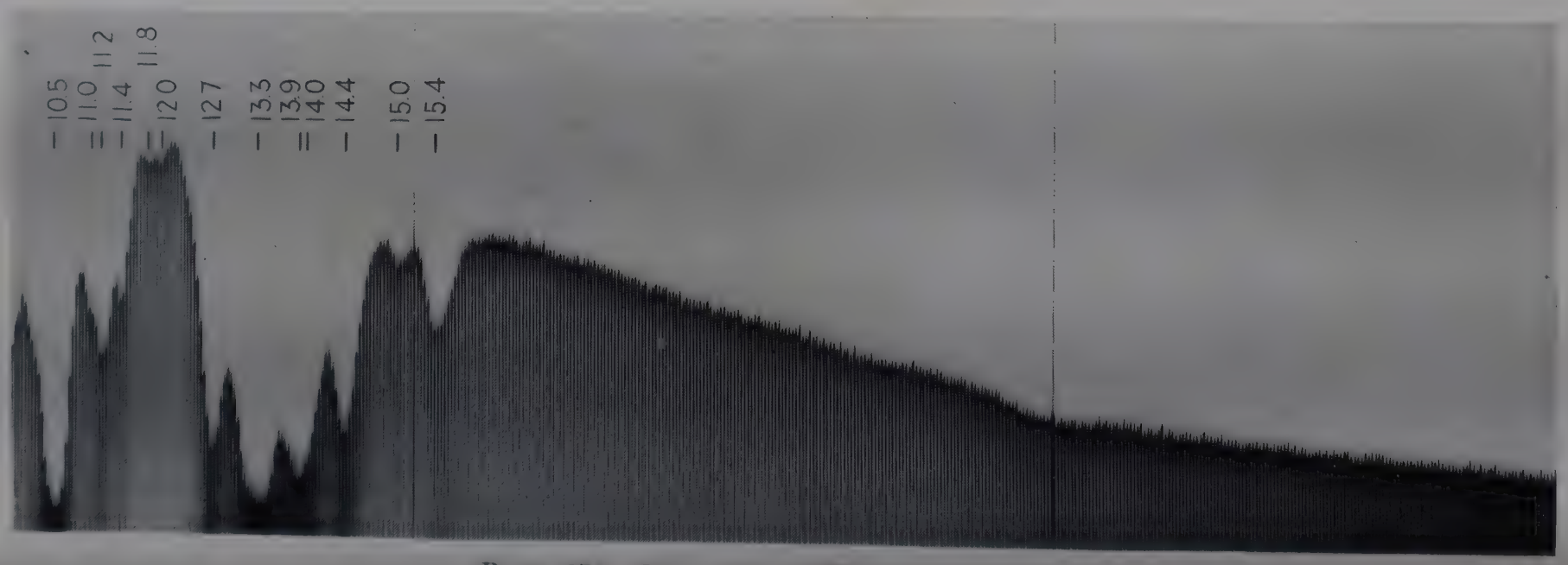


PLATE 275. Preparations: KBr prism, 0.15 mm.

METHYL n-BUTYL SULPHIDE

CH_3-S-$(CH_2)_3$-CH_3

(Both plates)

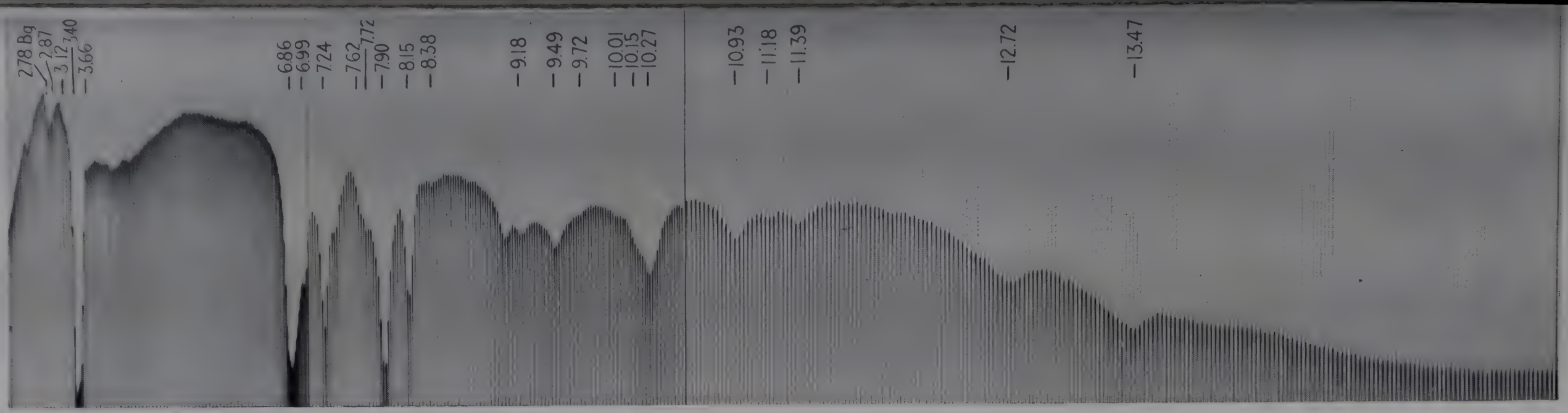
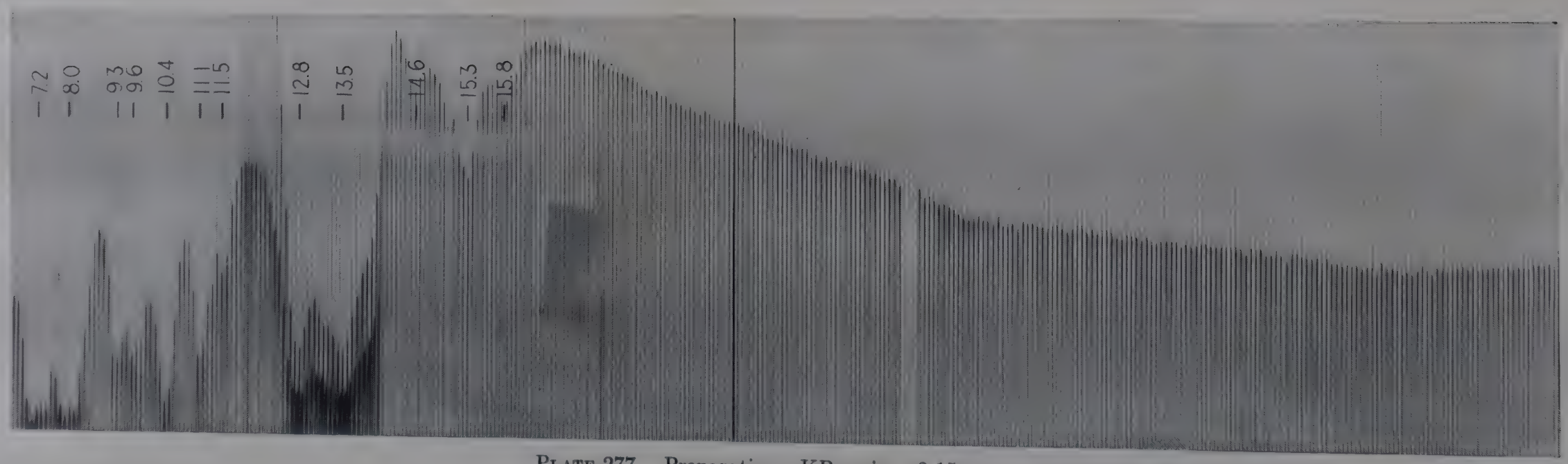


PLATE 276. Preparations: NaCl prism, 0.015 mm.



ETHYL n-BUTYL SULPHIDE

C_2H_5-S-$(CH_2)_3$-CH_3

(Both plates)

PLATE 277. Preparations: KBr prism, 0.15 mm.

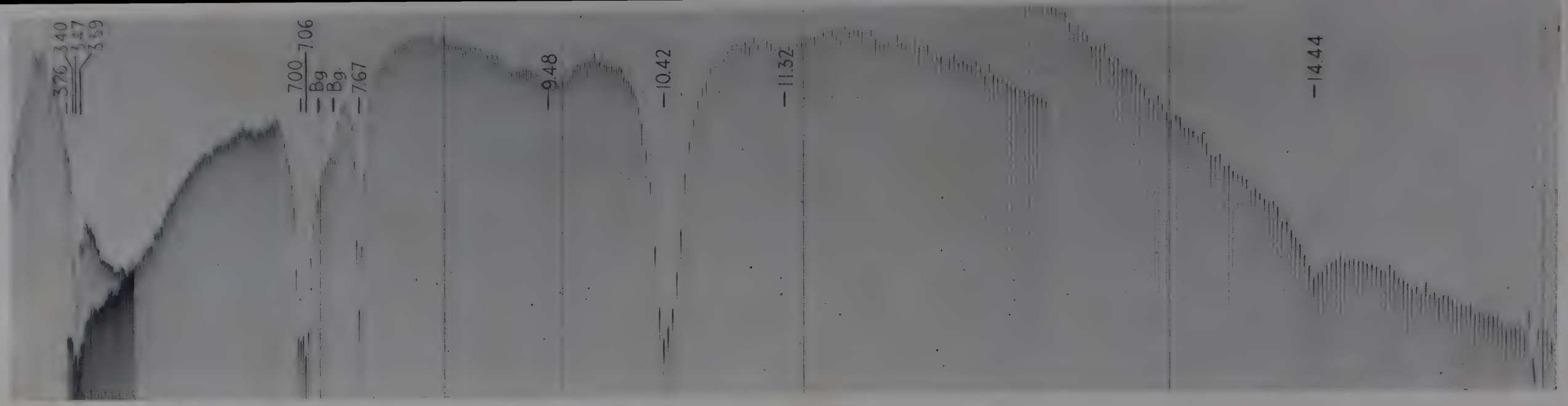
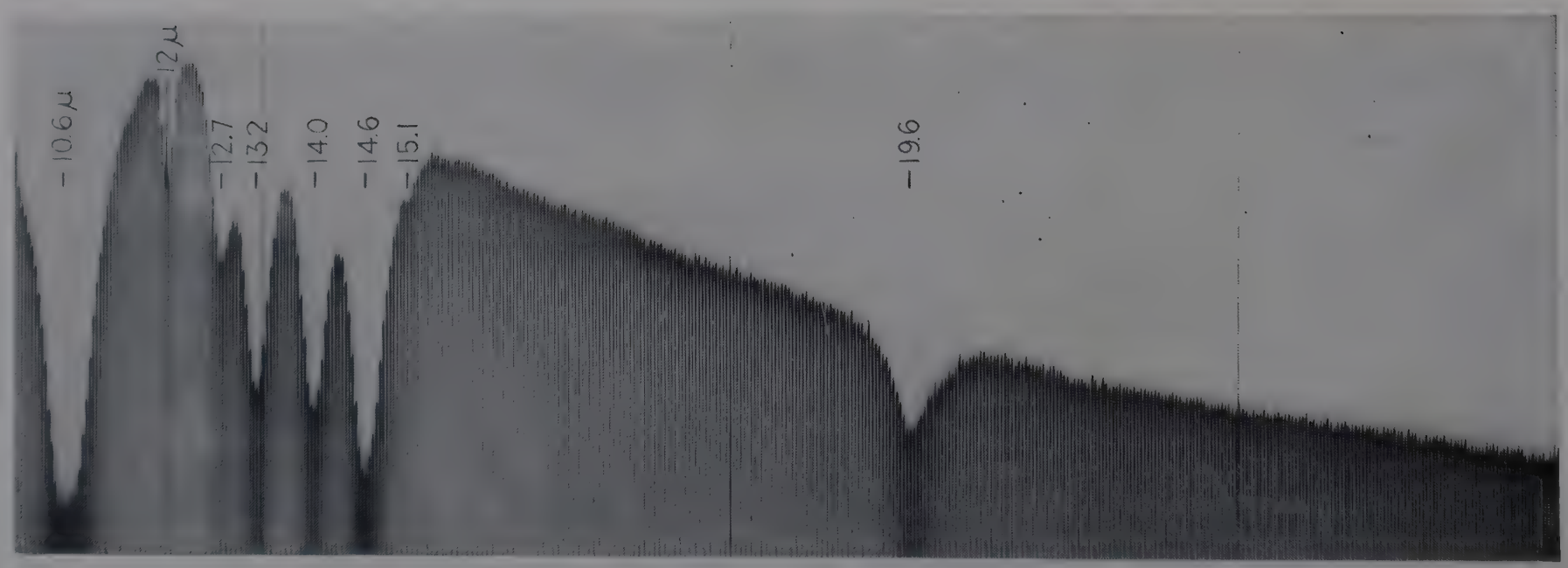


PLATE 278. Preparations: NaCl prism, 0.015 mm.



METHYL DISULPHIDE

CH_3-S-S-CH_3

(Both plates)

PLATE 279. Preparations: KBr prism, 0.15 mm.

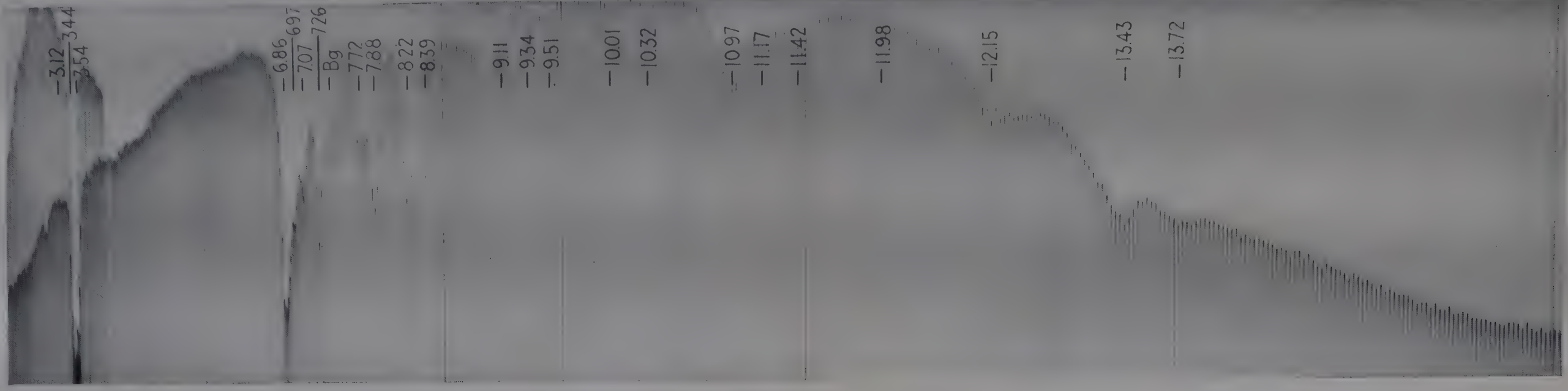


PLATE 280. Preparations: NaCl prism, 0.015 mm.

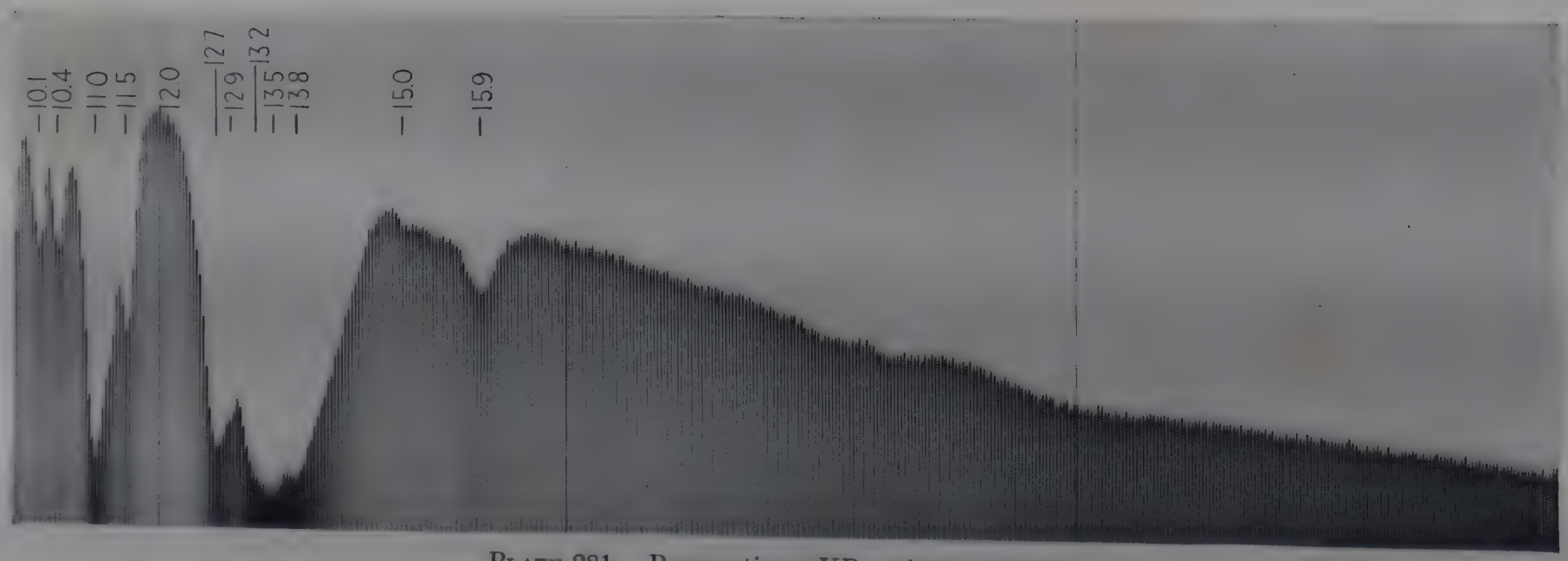
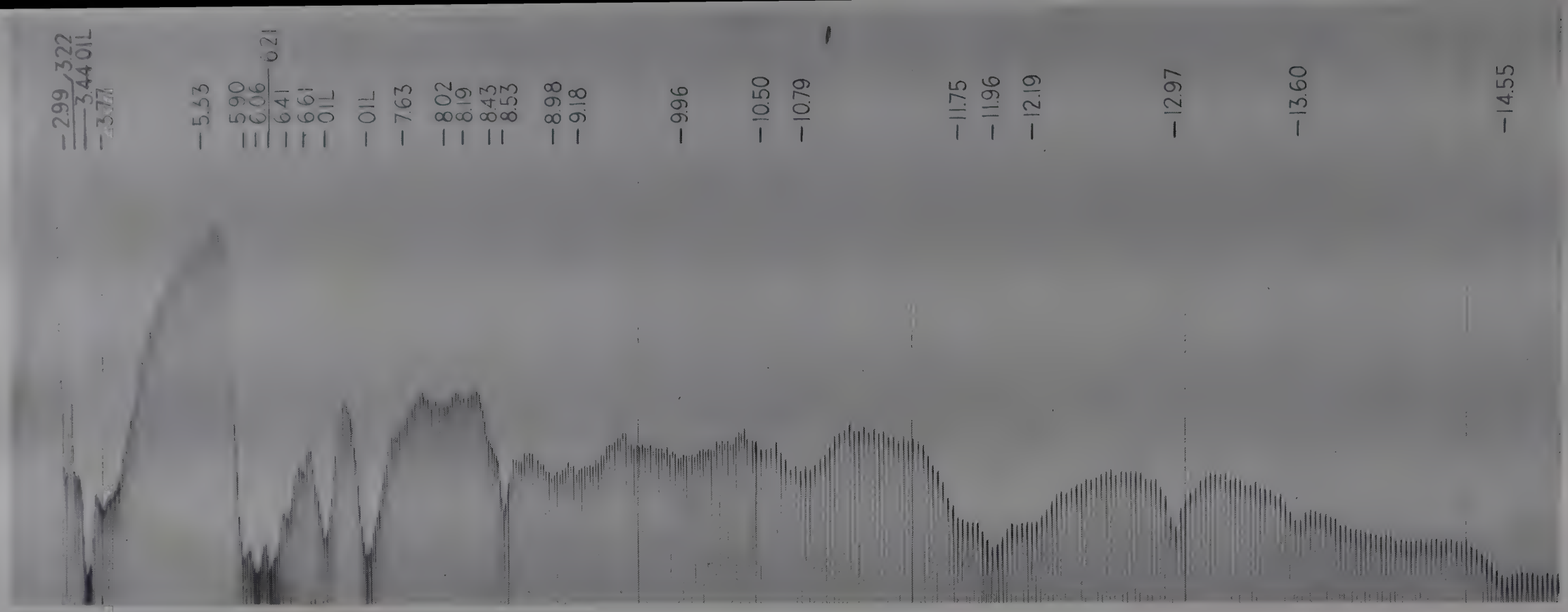


PLATE 281. Preparations: KBr prism, 0.15 mm.

n-BUTYL DISULPHIDE

$(CH_3)\cdot(CH_2)_3\text{-}S\text{-}S\text{-}(CH_2)_3\text{-}CH_3$

(Both plates)



GUANINE HYDROCHLORIDE

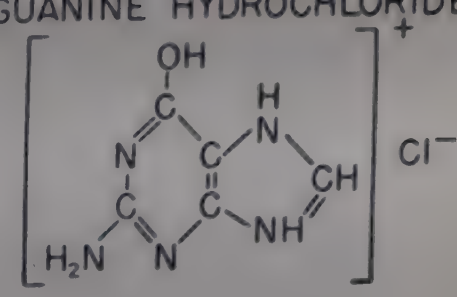
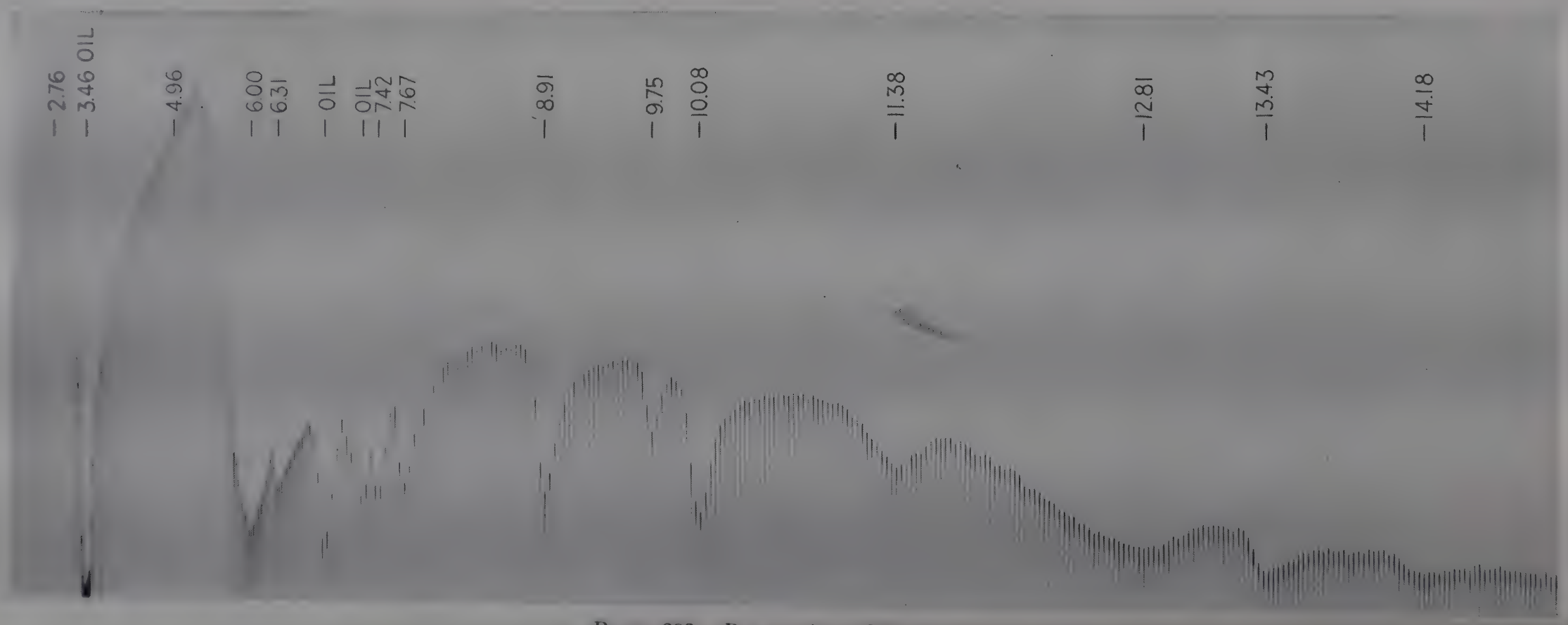


PLATE 282. Preparations: Oil paste



URIC ACID

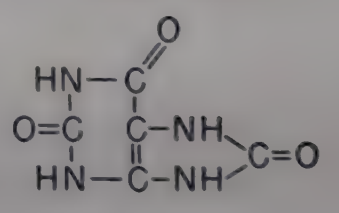
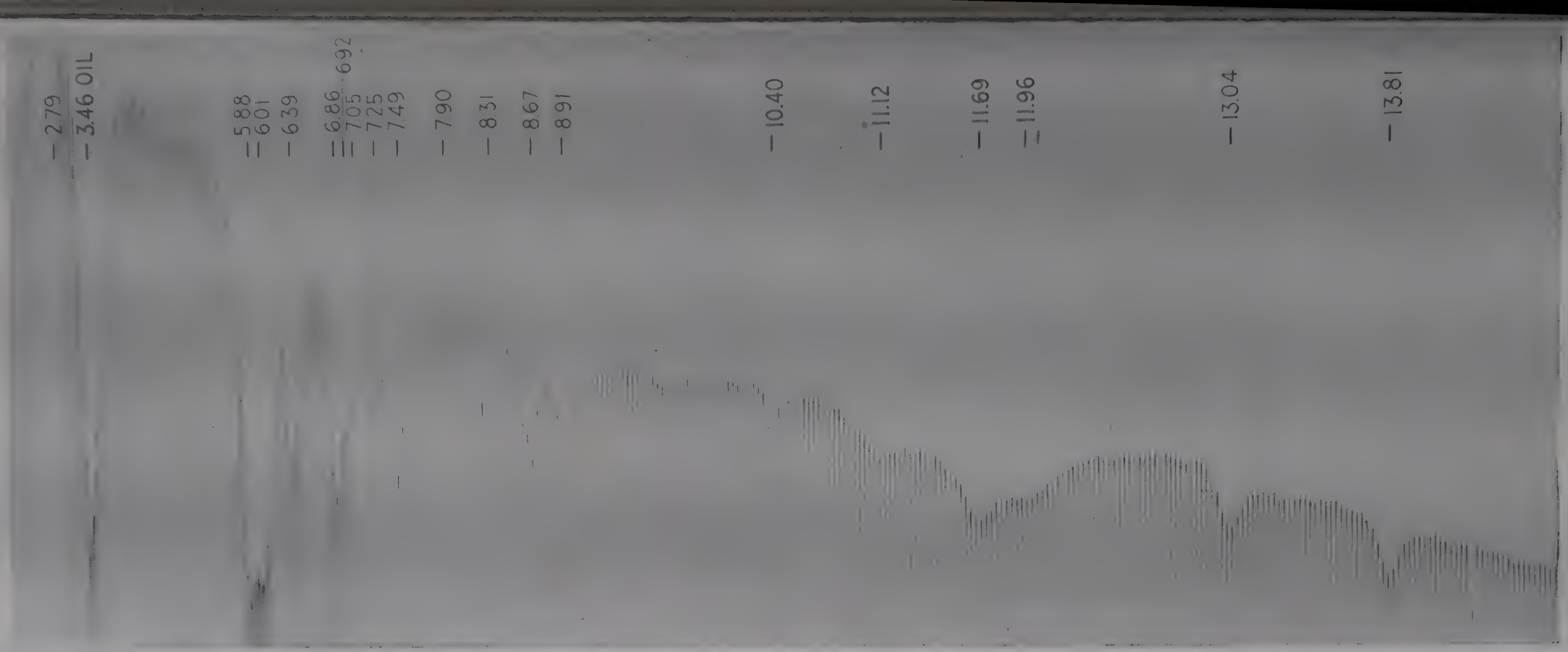


PLATE 283. Preparations: Oil paste



XANTHINE

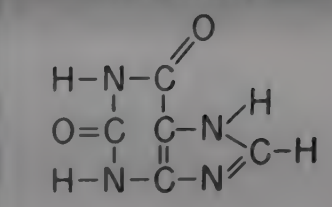
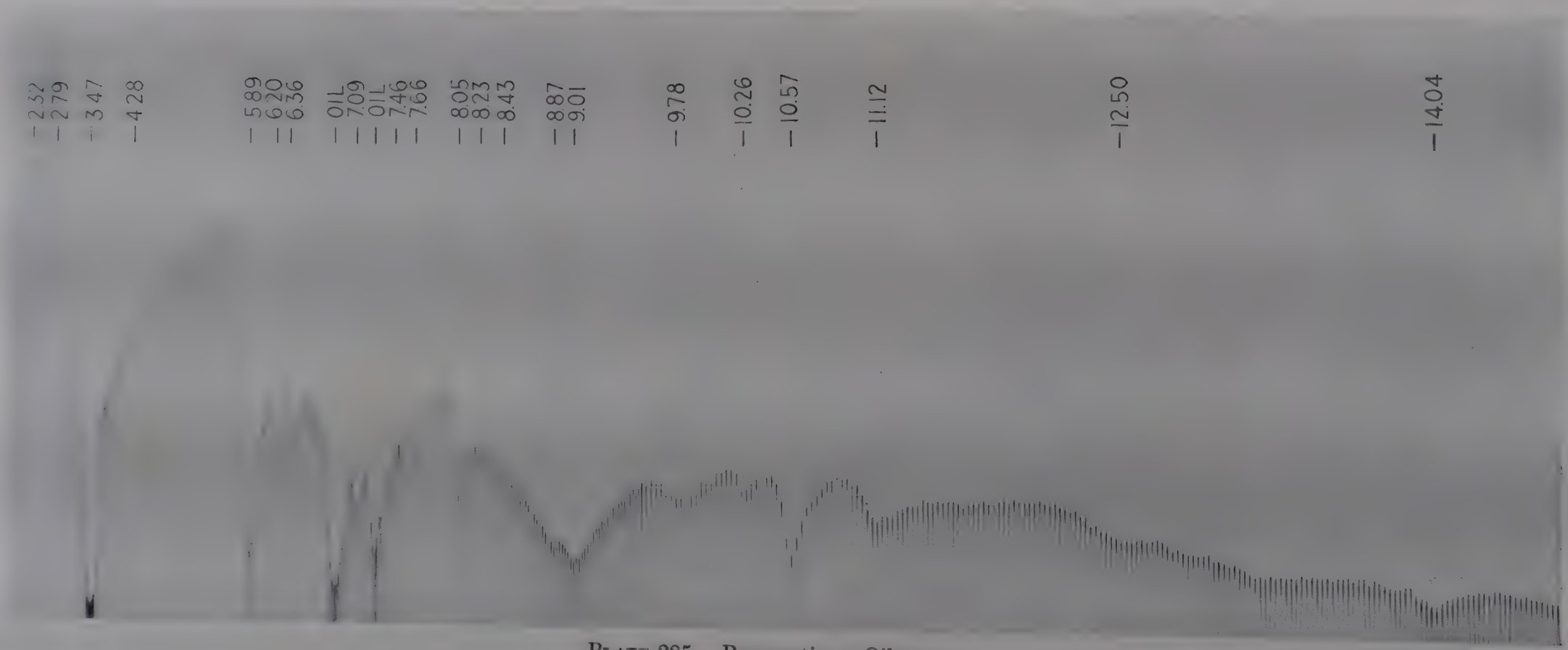


PLATE 284. Preparations: Oil paste



ADENINE SULPHATE

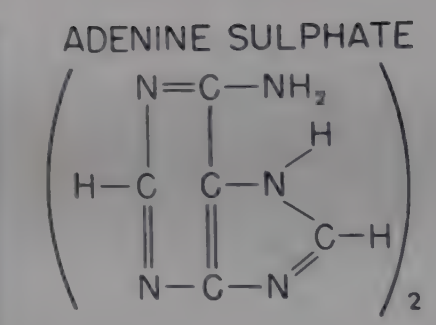


PLATE 285. Preparations: Oil paste

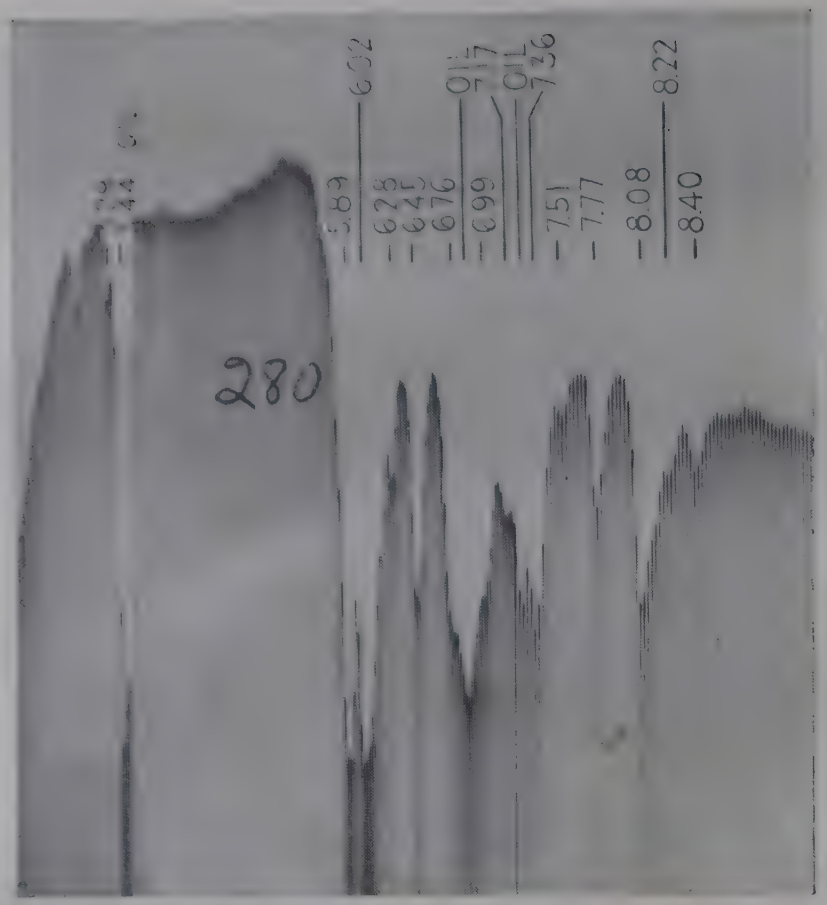
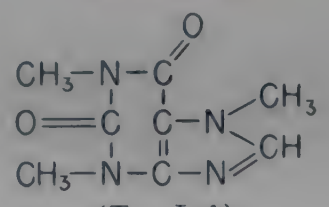


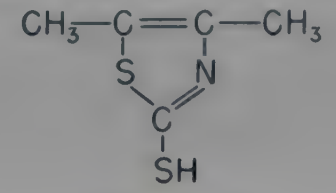
PLATE 286. Preparations: Oil paste

CAFFEINE



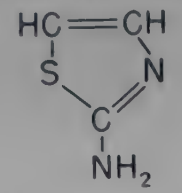
(*Top Left*)

2-MERCAPTO-4,5-DIMETHYL THIAZOLE



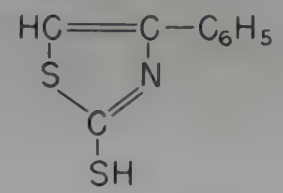
(*Top Right*)

2-AMINOTHIAZOLE



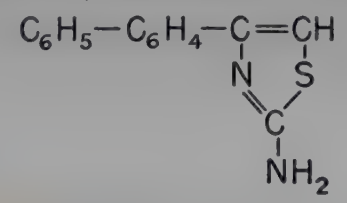
(*Bottom Left*)

2-MERCAPTO-4-PHENYLTHIAZOLE



(*Bottom Right*)

2-AMINO-4-(*p*-BIPHENYL) THIAZOLE



(*Bottom Center*)

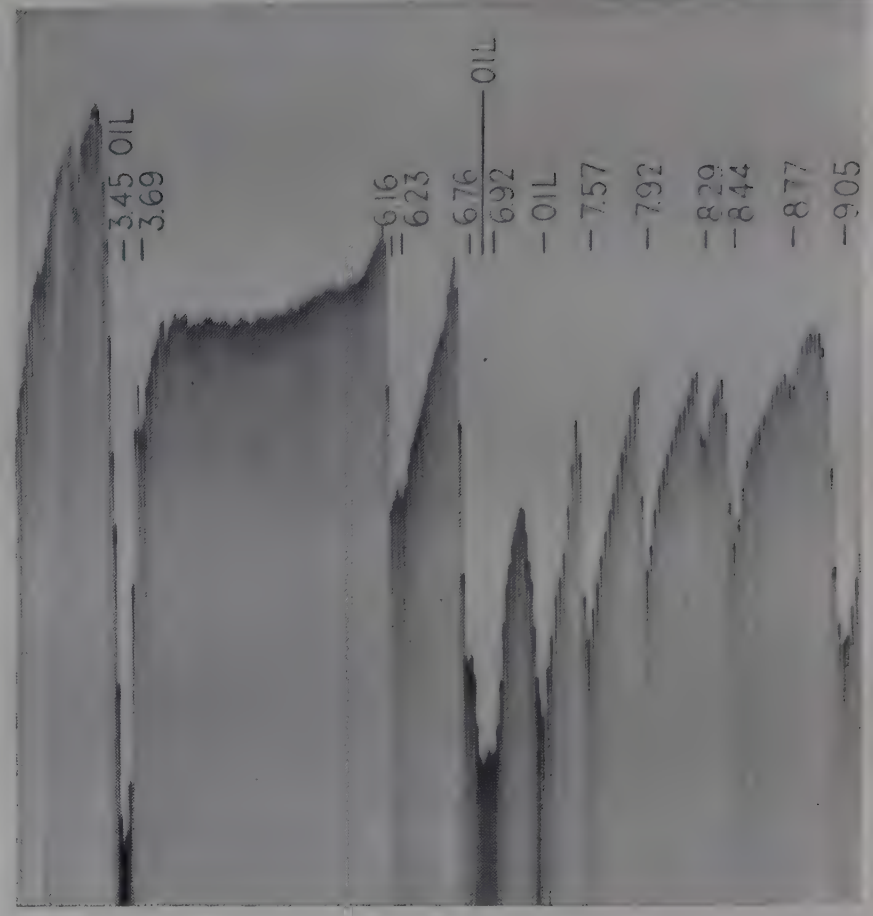


PLATE 287. Assignments: 6.16 μ Thiazole I
6.76 μ Thiazole II
Preparations: Oil paste

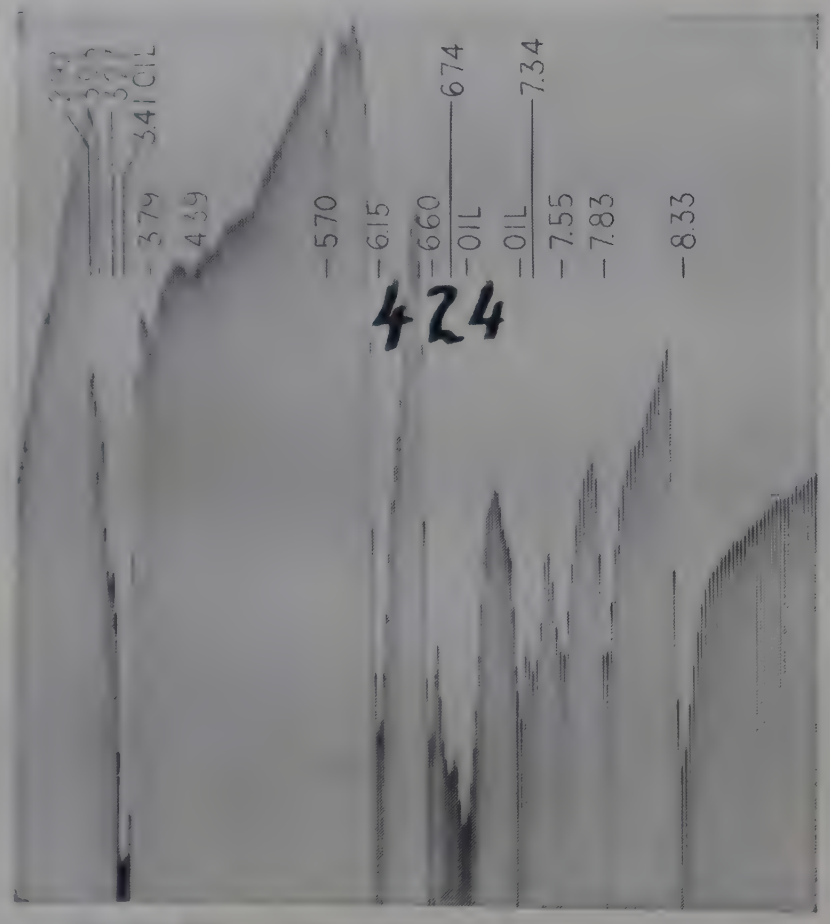


PLATE 288. Assignments: 6.15 μ Thiazole I
6.60 μ Thiazole II
Preparations: Oil paste

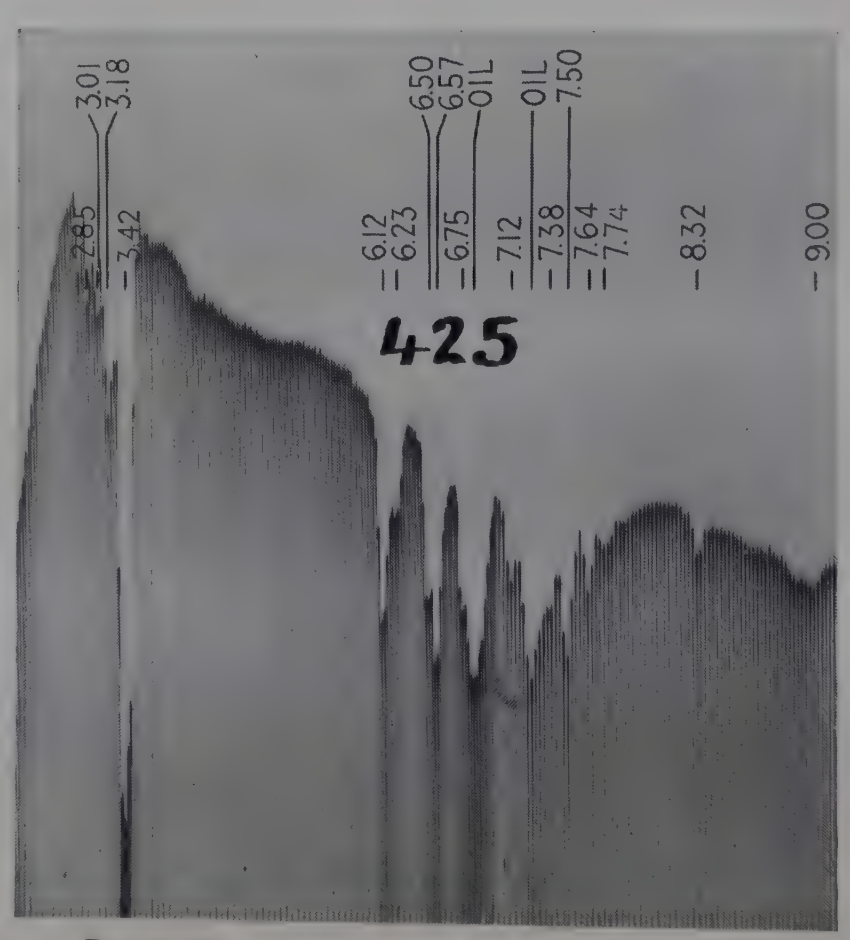


PLATE 289. Assignments: 6.12 μ Thiazole I
6.50 μ Thiazole II
Preparations: Oil paste

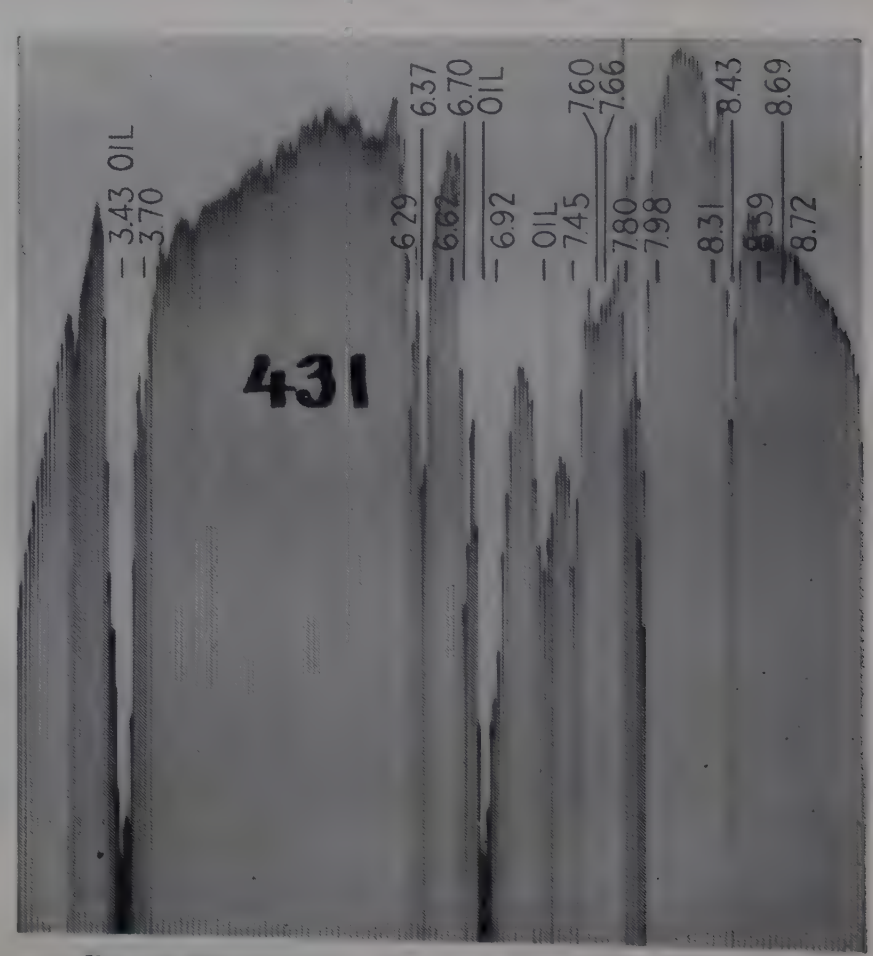


PLATE 290. Assignments: 6.29 μ Unassigned
6.37 μ Thiazole I
6.70 μ Thiazole II

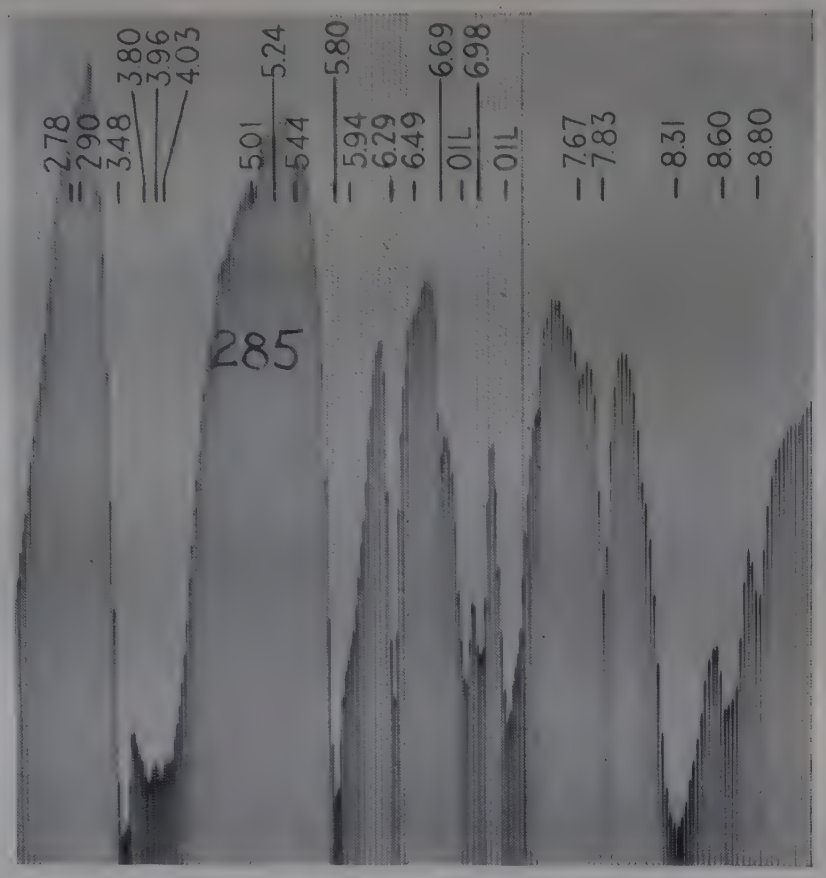
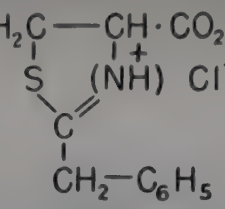


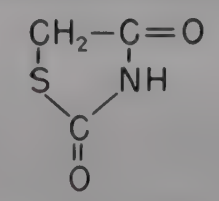
PLATE 291. Assignments: 5.80 μ Acid C=O
6.29 μ C=N
Preparations: Oil paste

2-BENZYL-Δ^2-THIAZOLINE-4-CARBOXYLIC ACID HYDROCHLORIDE



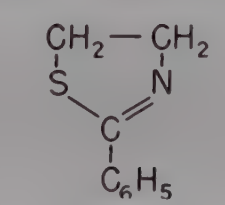
(Top Left)

2,4-DIOXOTHIAZOLIDINE



(Top Right)

2-PHENYLTHIAZOLINE-Δ^2



(Bottom)

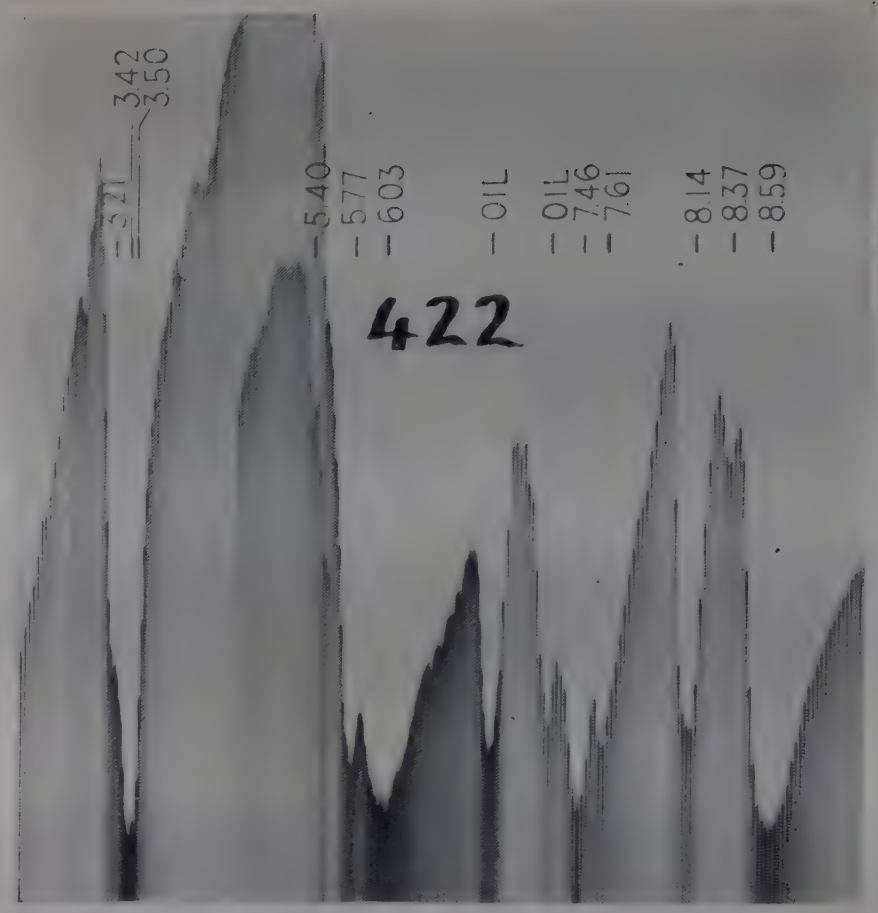


PLATE 294. Assignments: 5.77 μ 4-C=O
6.03 μ 2-C=O
Preparations: Oil paste

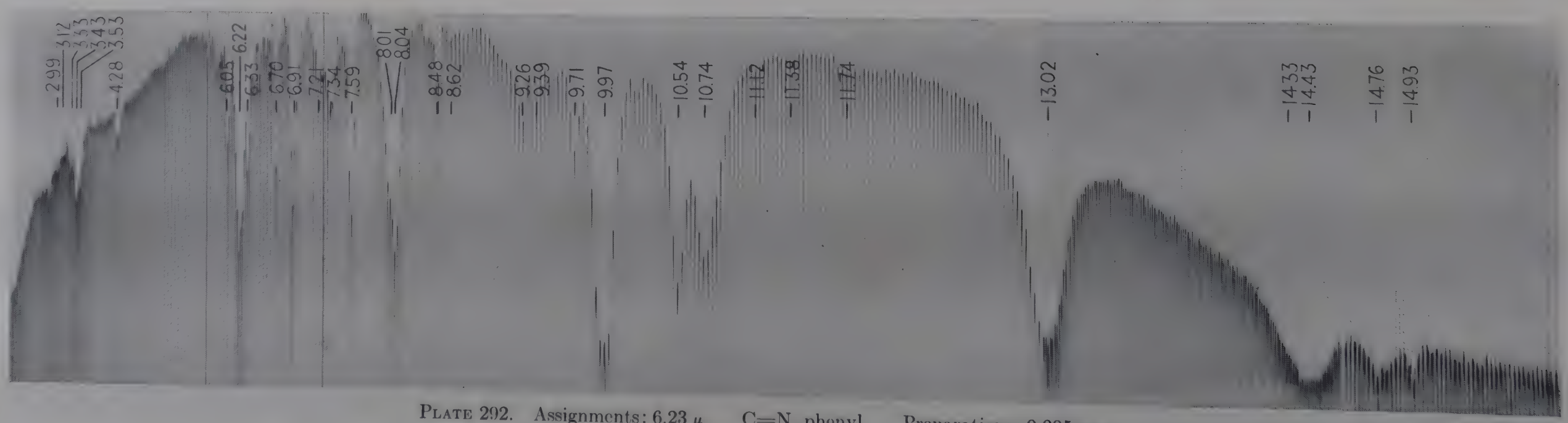
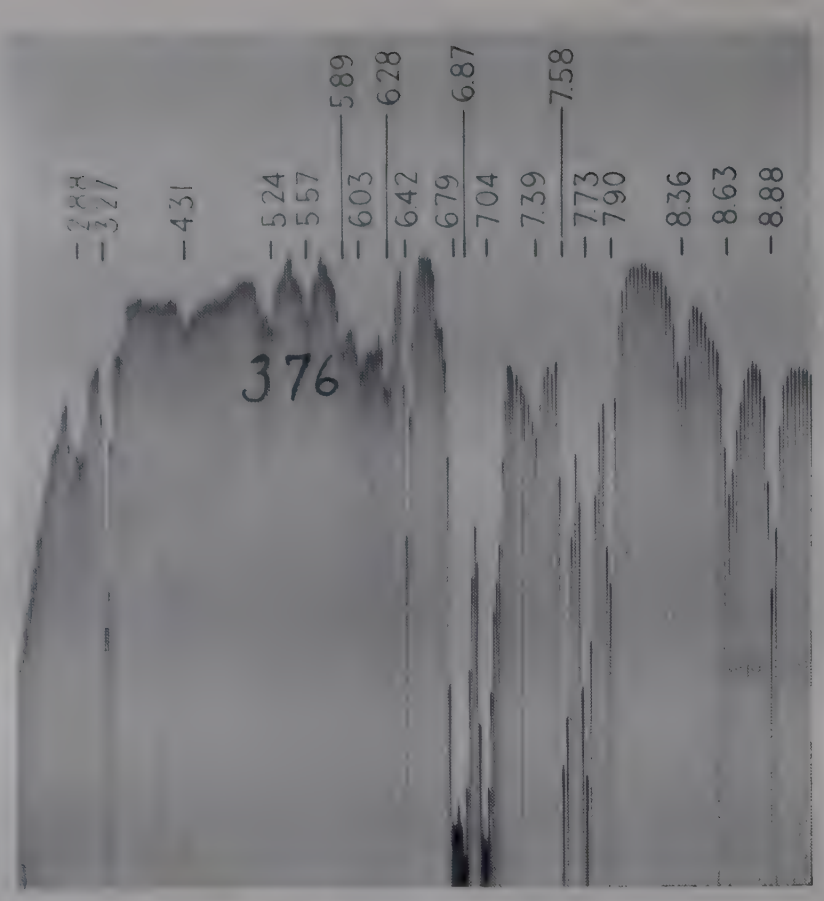
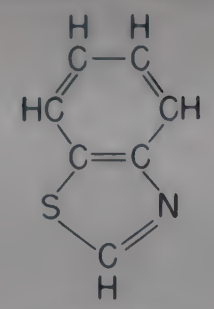


PLATE 292. Assignments: 6.23 μ C=N, phenyl Preparations: 0.005 mm.
6.33 μ } Phenyl

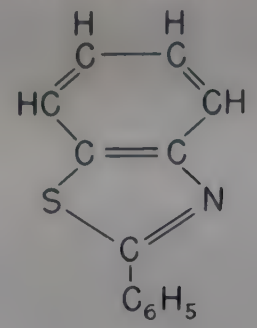


BENZOTHIAZOLE



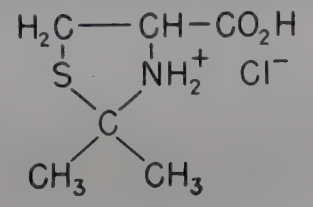
(*Top Left*)

2-PHENYLBENZOTHIAZOLE



(*Top Right*)

2,2-DIMETHYLTHIAZOLIDINE-4-CARBOXYLIC ACID HYDROCHLORIDE



(*Bottom*)

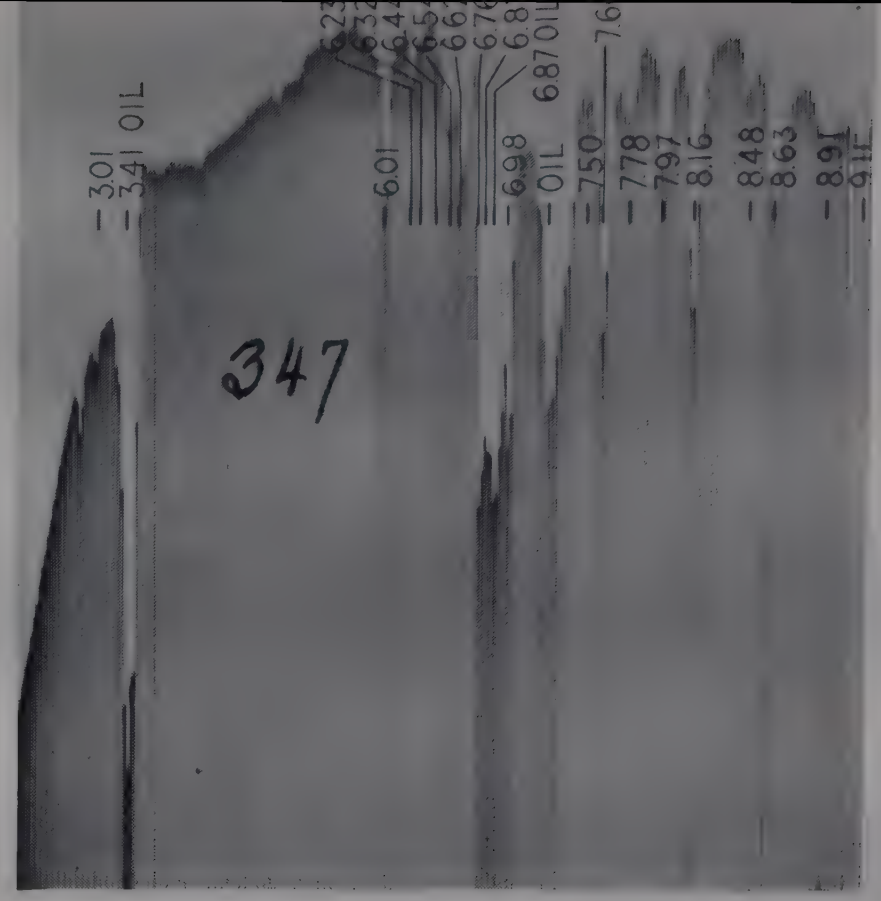


PLATE 295. Preparations: 0.02 mm.

PLATE 296. Preparations: Oil paste

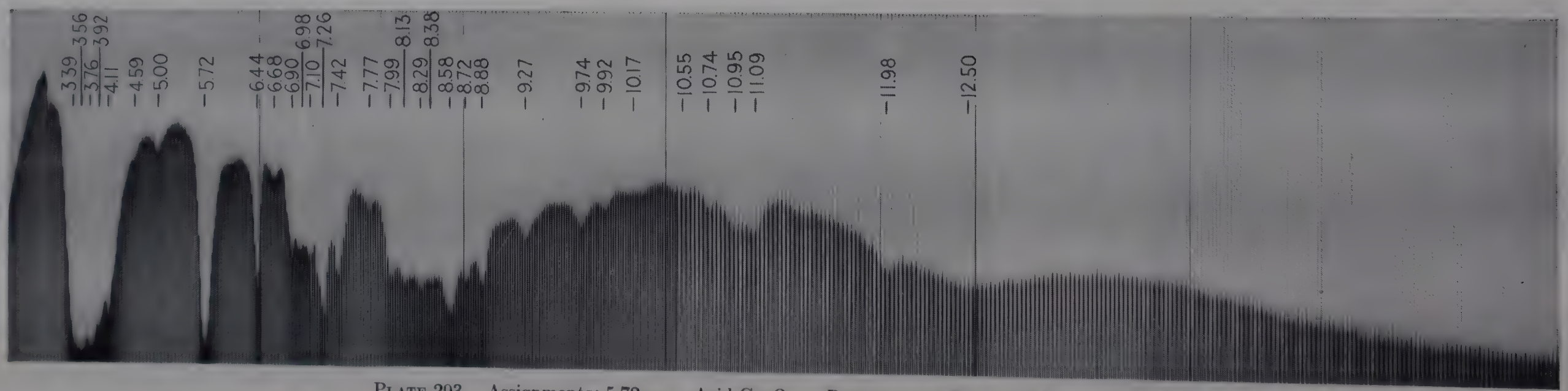


PLATE 293. Assignments: 5.72 μ Acid C=O Preparations: Deposited from methanol
6.44 μ δNH_2

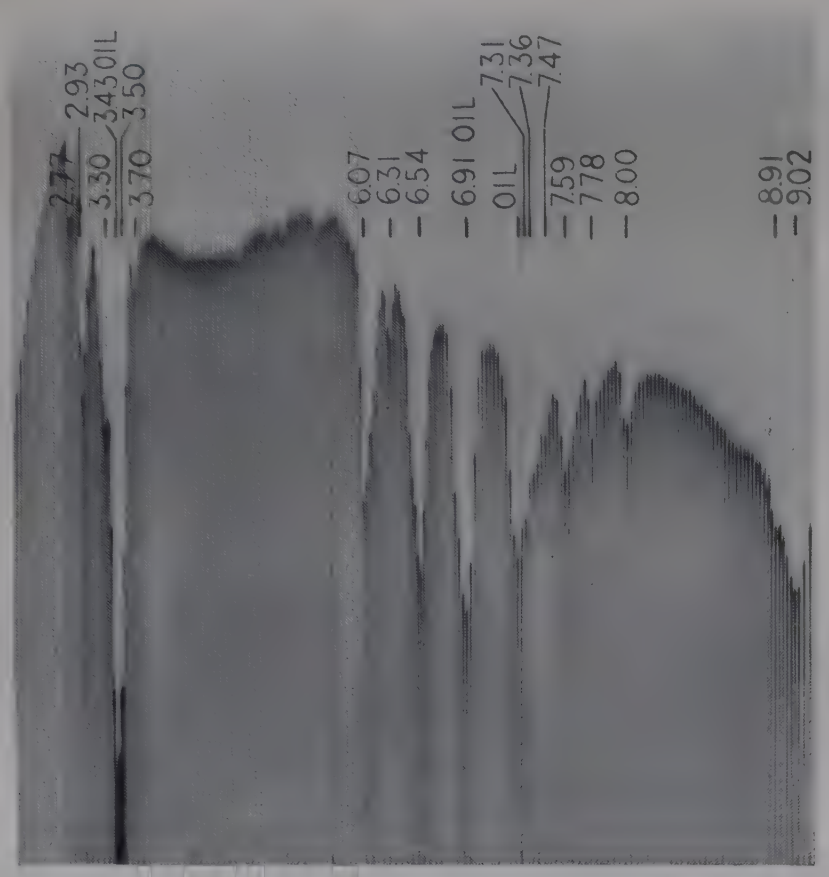
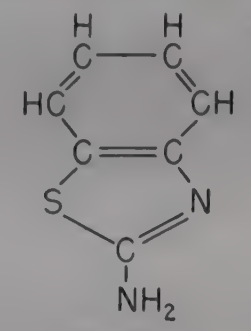


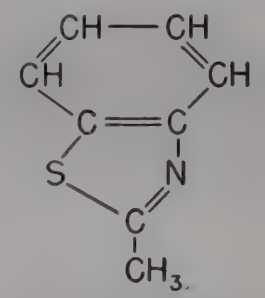
PLATE 297. Preparations: Oil paste

2-AMINOBENZOTHIAZOLE



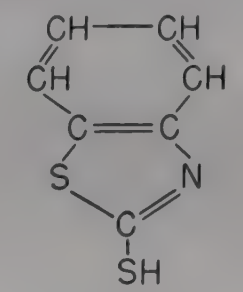
(Top Left)

2-METHYLBENZOTHIAZOLE



(Bottom)

2-MERCAPTOBENZOTHIAZOLE



(Top Right)

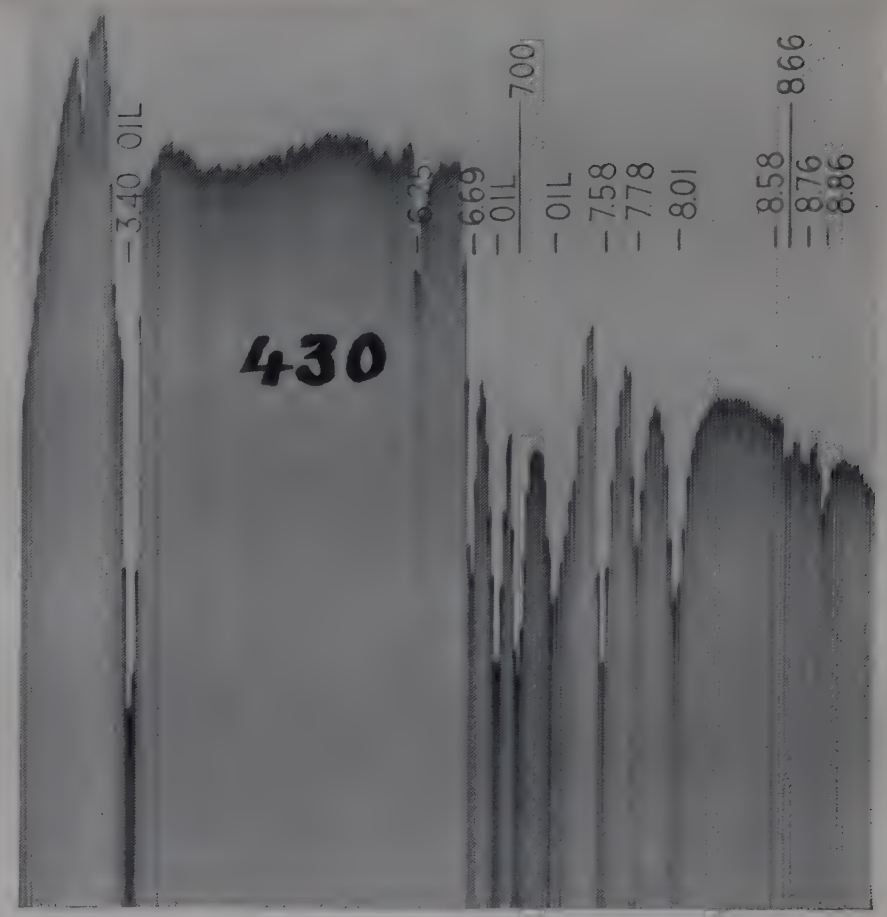


PLATE 299. Preparations: Oil paste

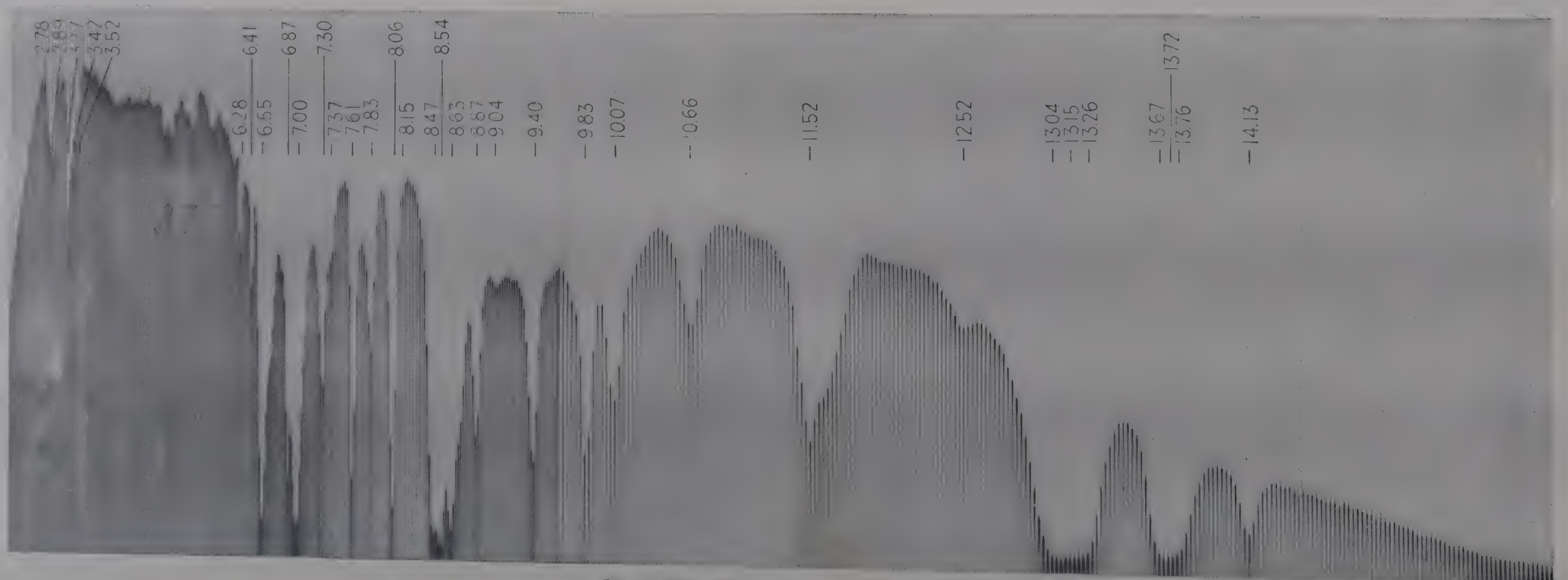


PLATE 298. Preparations: 0.02 mm

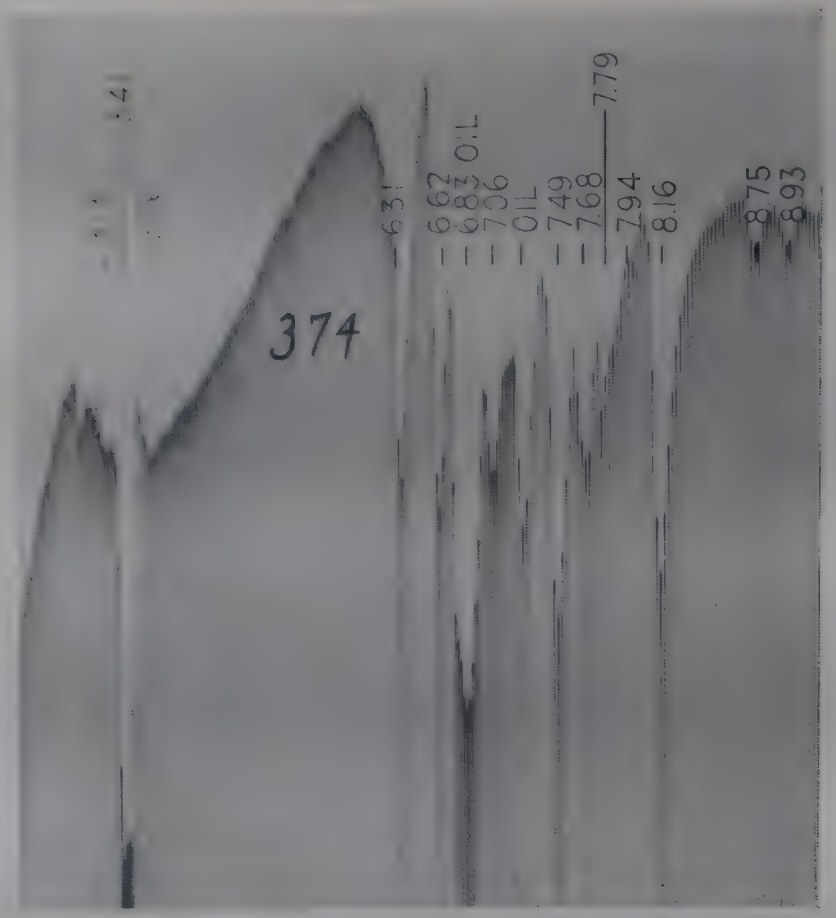
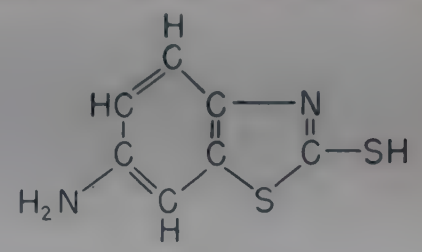


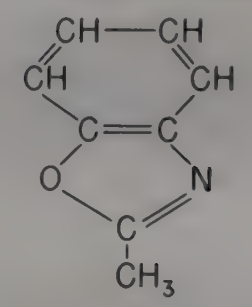
PLATE 300. Preparations: Oil paste

6-AMINO-2-MERCAPTOBENZOTHIAZOLE



(Top Left)

2-METHYLBENZOXAZOLE



(Bottom)

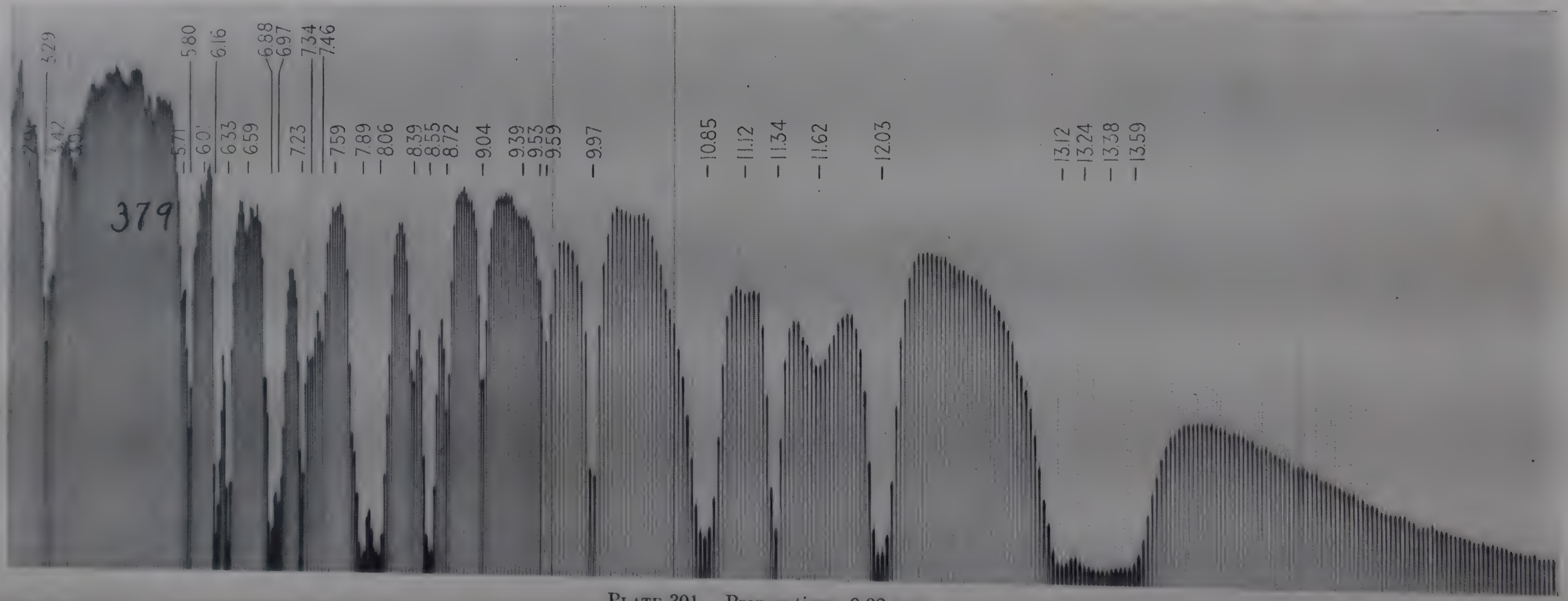
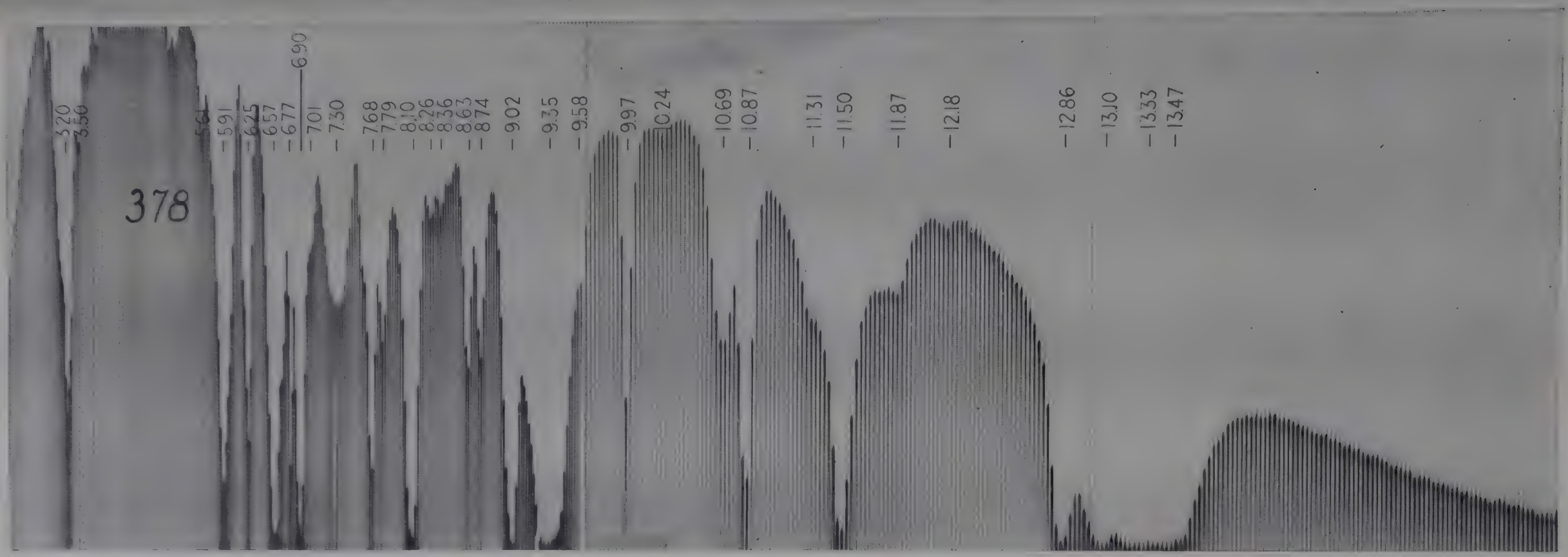


PLATE 301. Preparations: 0.02 mm.



BENZOXAZOLE

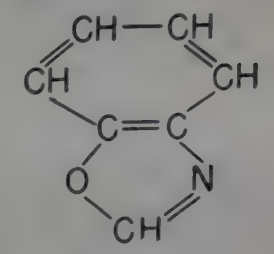
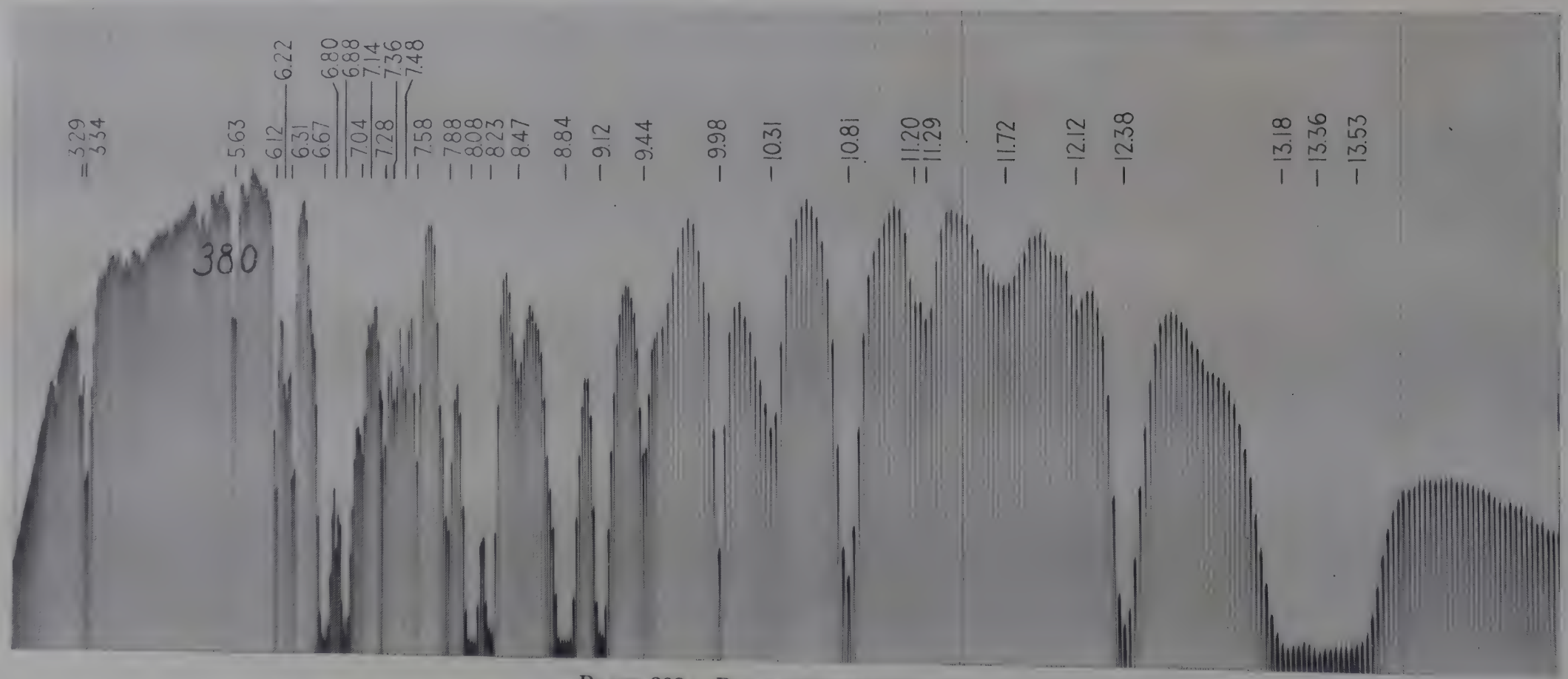


PLATE 302. Preparations: 0.02 mm.



2-ETHYLMERCAPTOBENZOXAZOLE

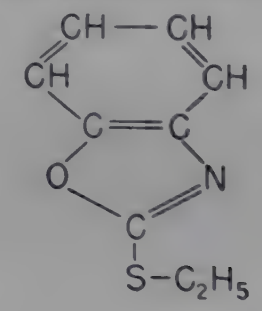
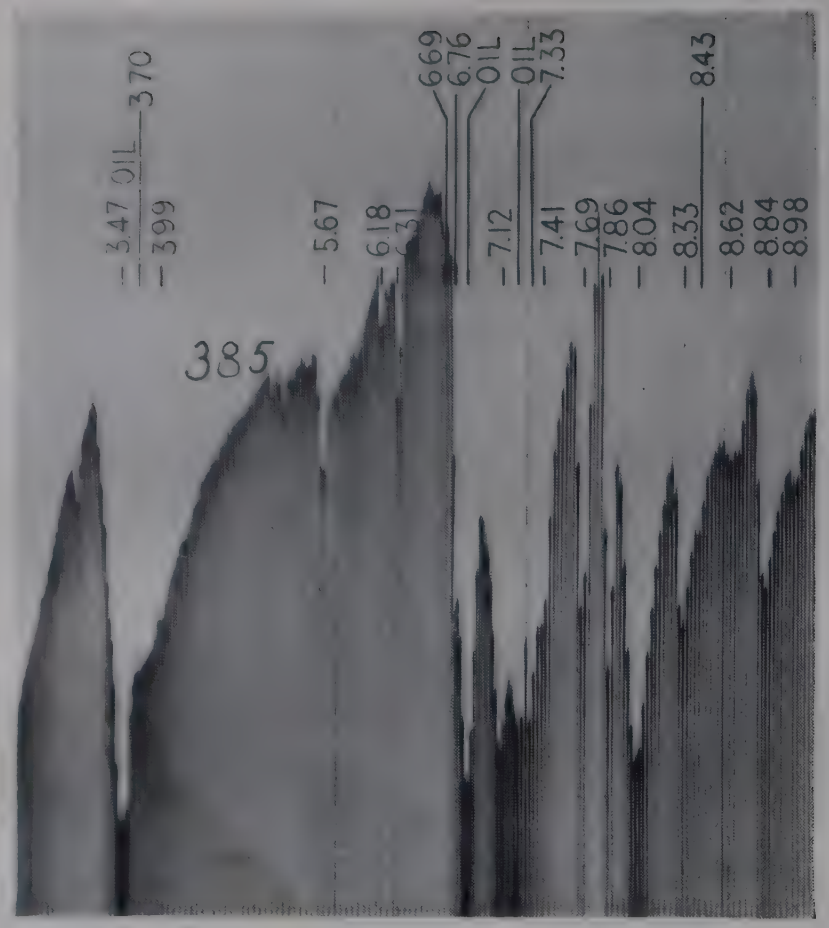


PLATE 303. Preparations: 0.02 mm.



BENZIMIDAZOLE

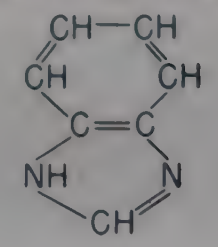
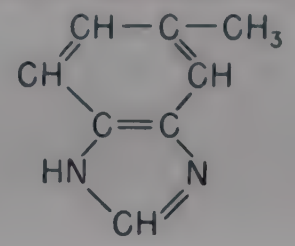


Plate 304. Preparations: Oil paste

5-METHYLBENZIMIDAZOLE



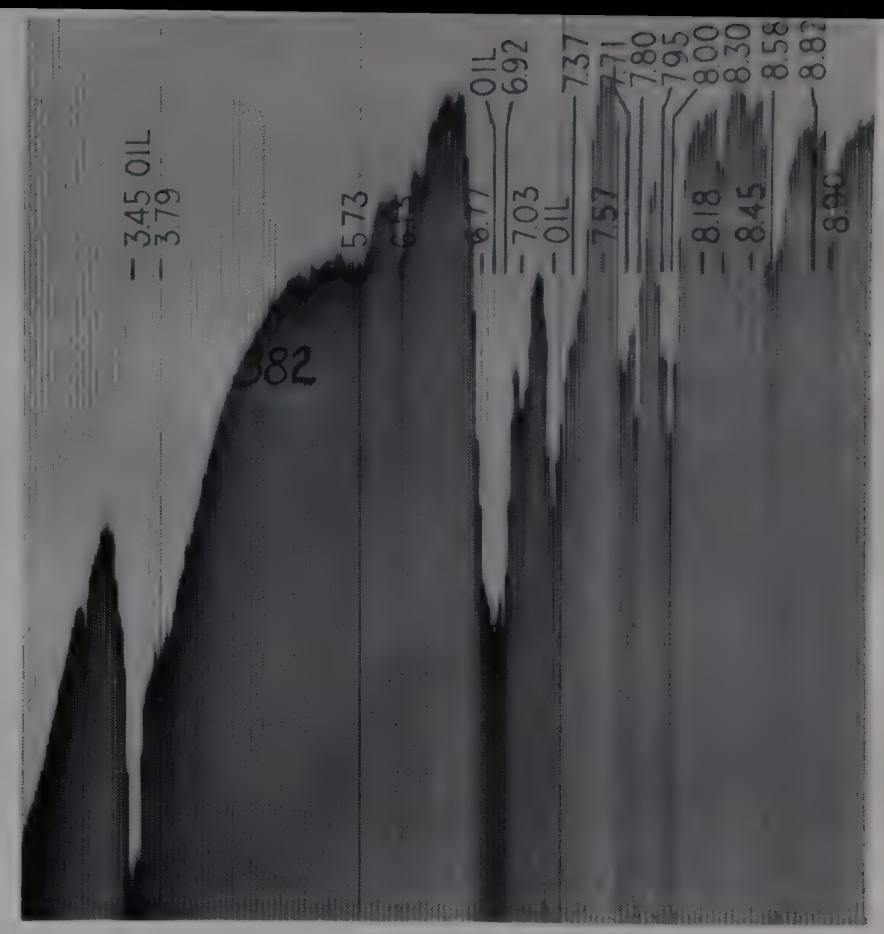
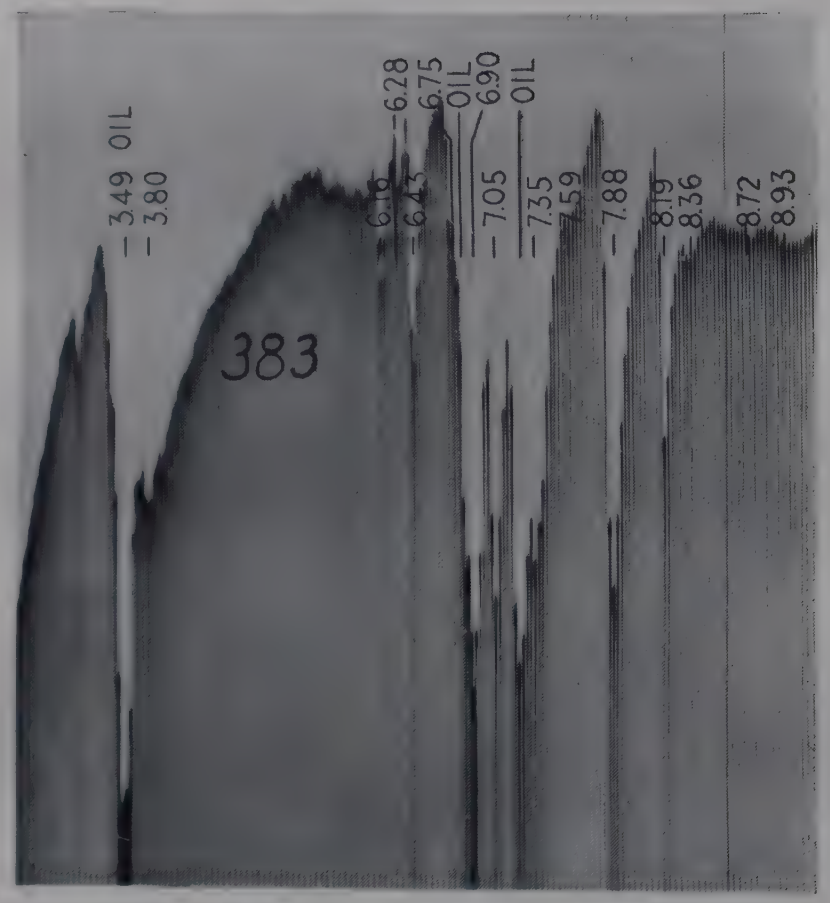


Plate 305. Preparations: Oil paste



2-METHYLBENZIMIDAZOLE

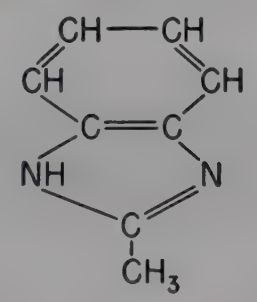
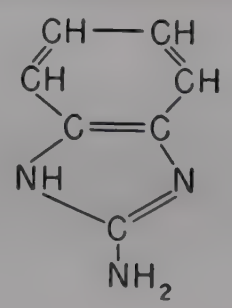


Plate 306. Preparations: Oil paste

2-AMINOBENZIMIDAZOLE



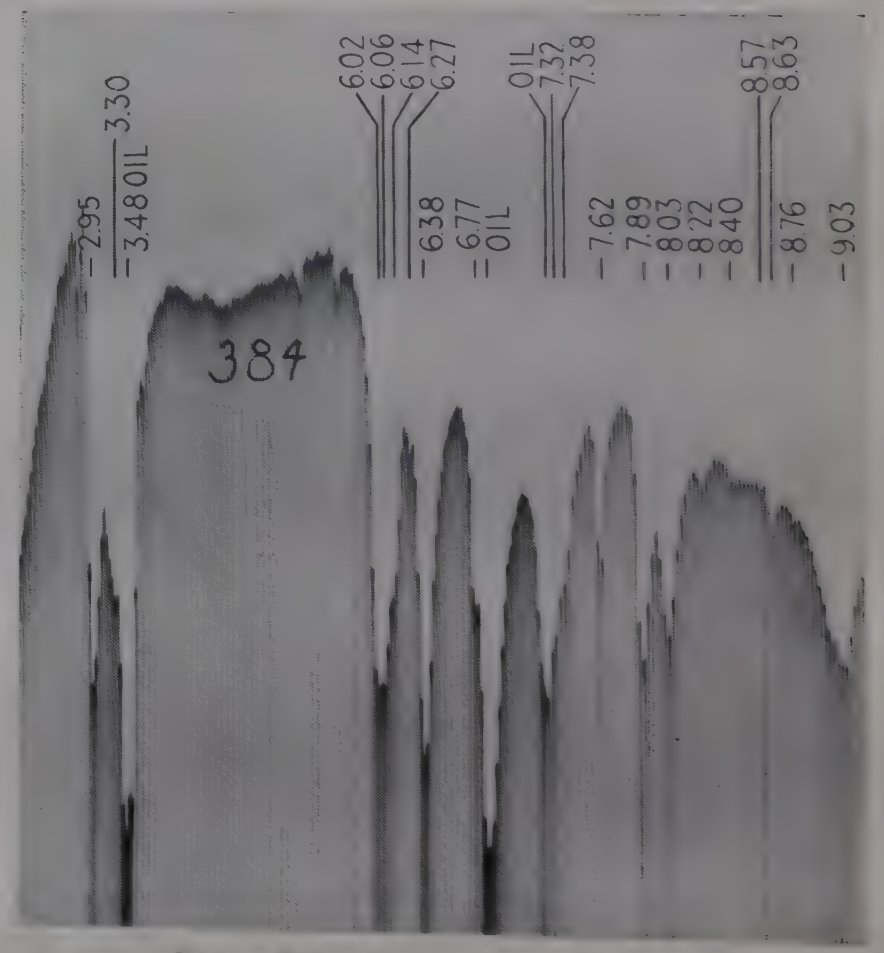


Plate 307. Preparations: Oil paste

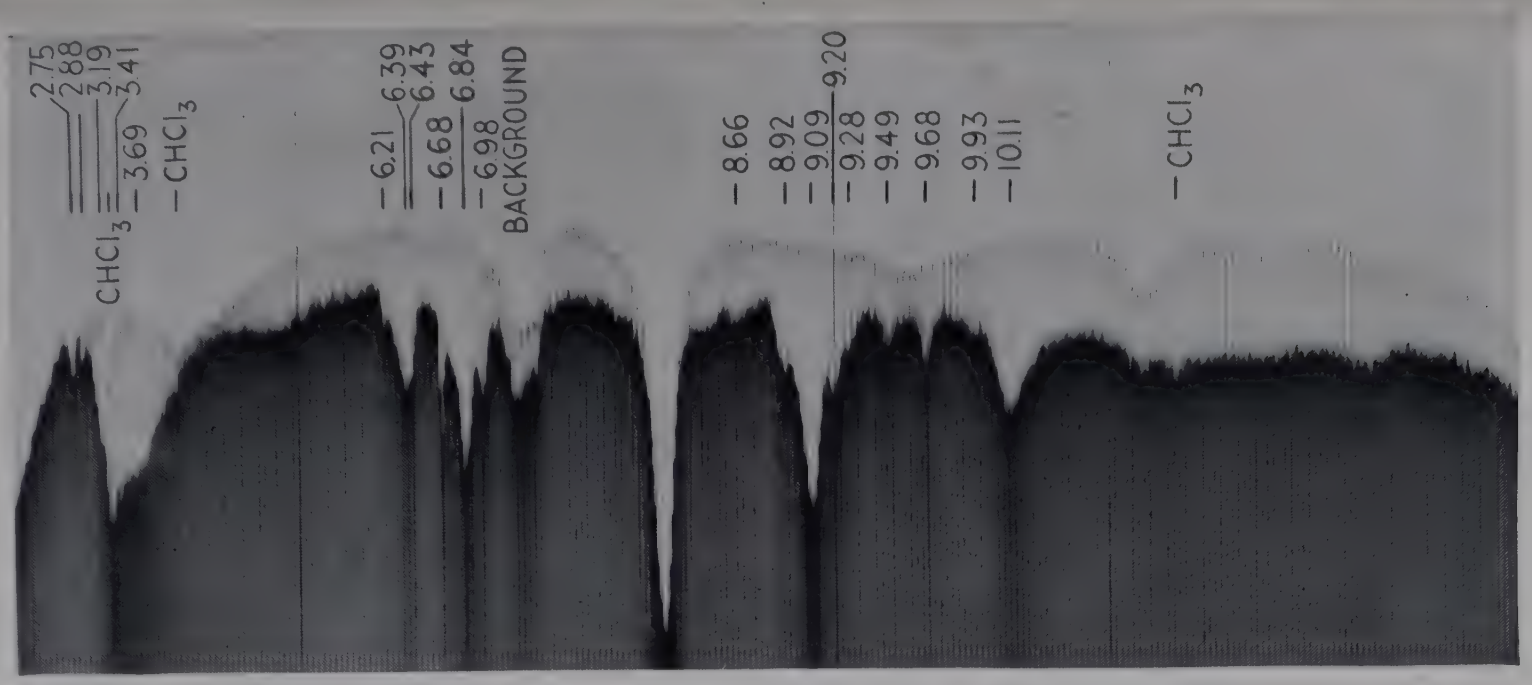
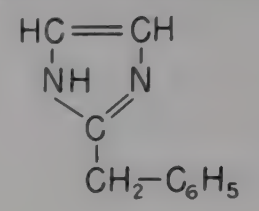


PLATE 308a. Preparations: Saturated solution in $CHCl_3$, 0.015 mm.

2-BENZYLIMIDAZOLE-Δ^1



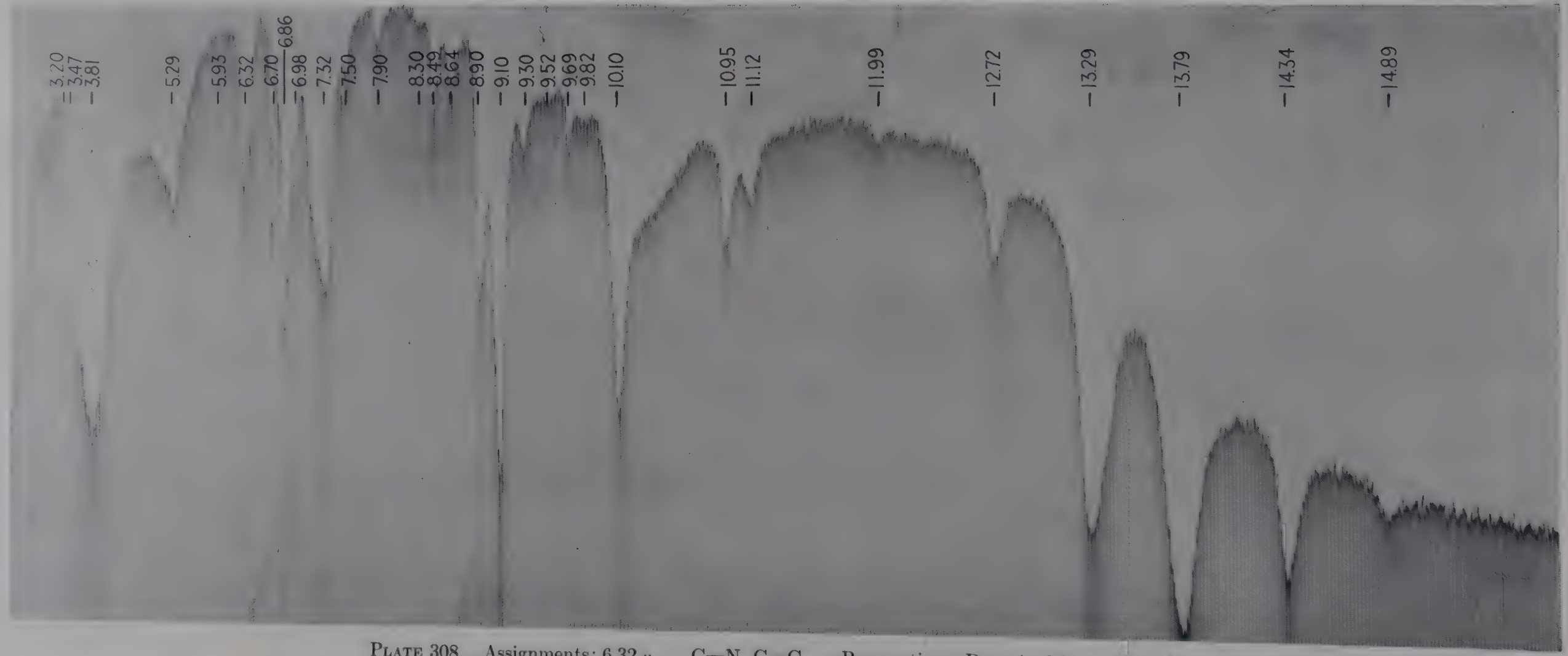


PLATE 308. Assignments: 6.32 μ C=N, C=C Preparations: Deposited f

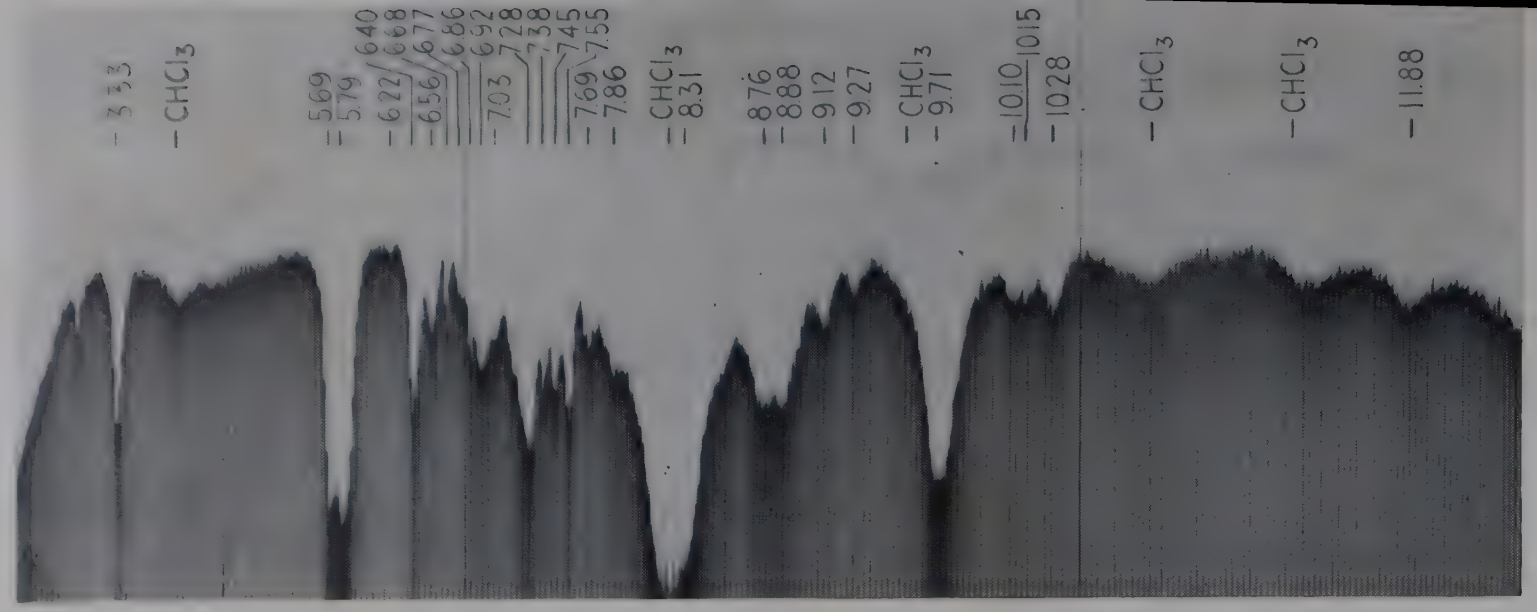
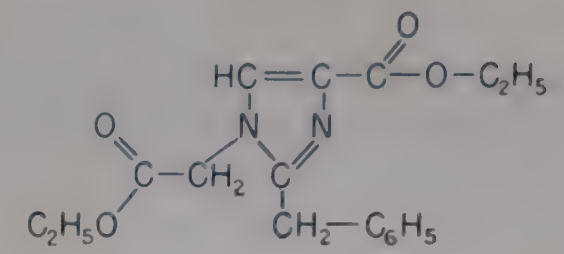


PLATE 309a. Assignments: 5.69 μ Acetic ester C=O
5.79 μ Carboxylic ester C=O
6.40 μ C=N

Preparations: Saturated solution in $CHCl_3$, 0.015 mm.

2-BENZYL-4-CARBETHOXYIMIDAZOLE-1-ACETIC ACID ETHYL ESTER



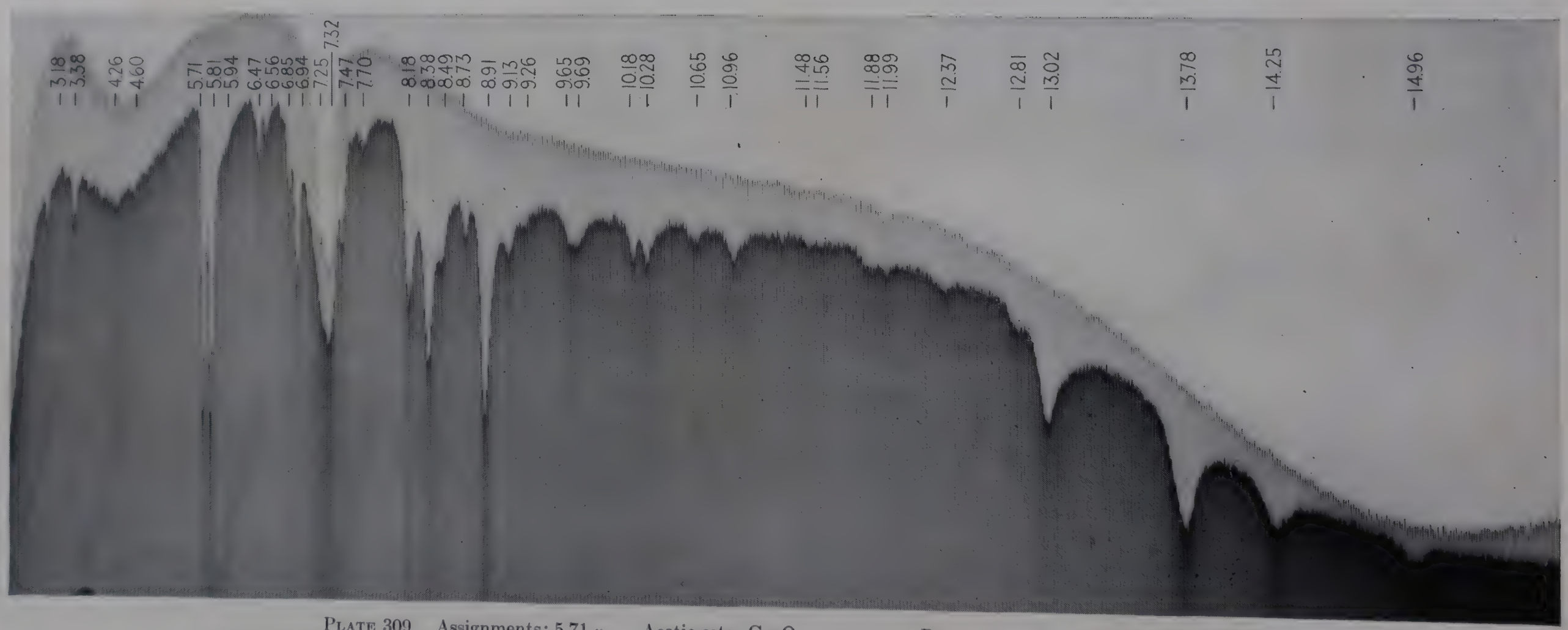
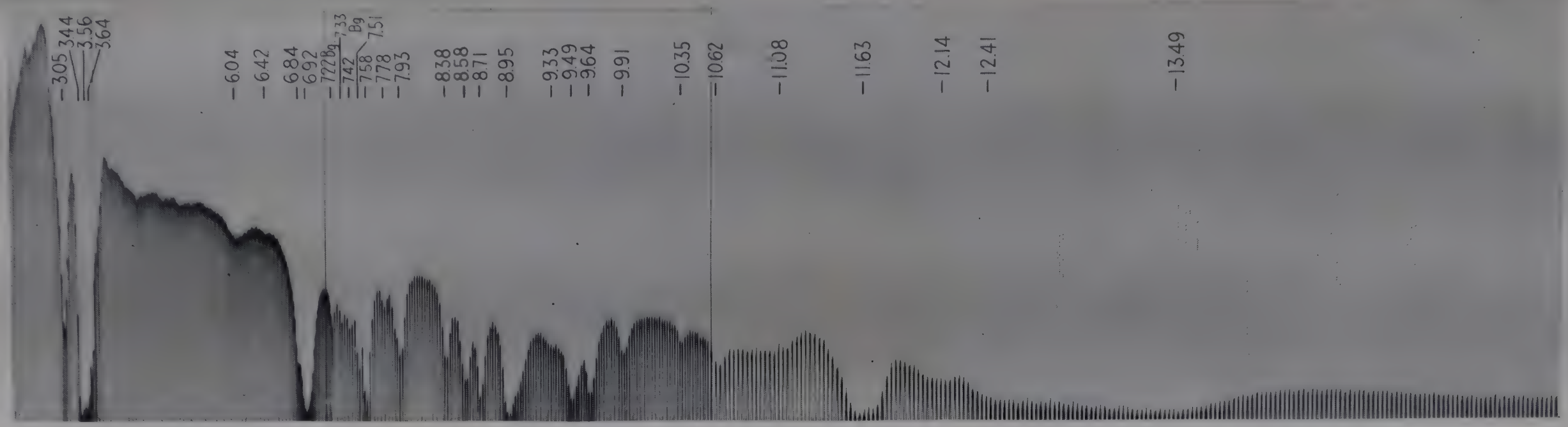


PLATE 309. Assignments: 5.71 μ Acetic ester C=O
5.81 μ Carboxylic ester conjugated
6.47 μ C=N

Preparations: Deposited from CCl_4



PIPERIDINE

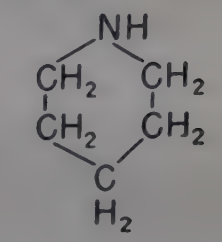
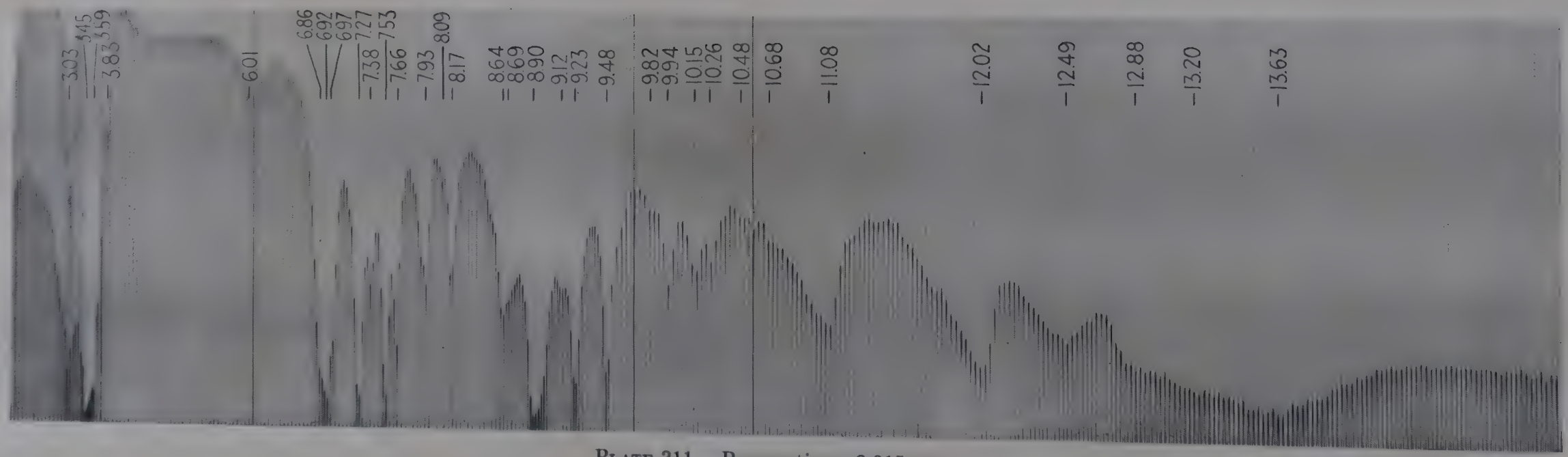


PLATE 310. Preparations: 0.015 mm.



α-METHYLPIPERIDINE

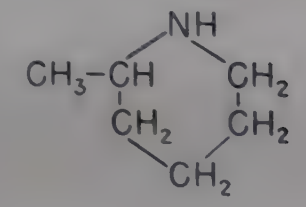
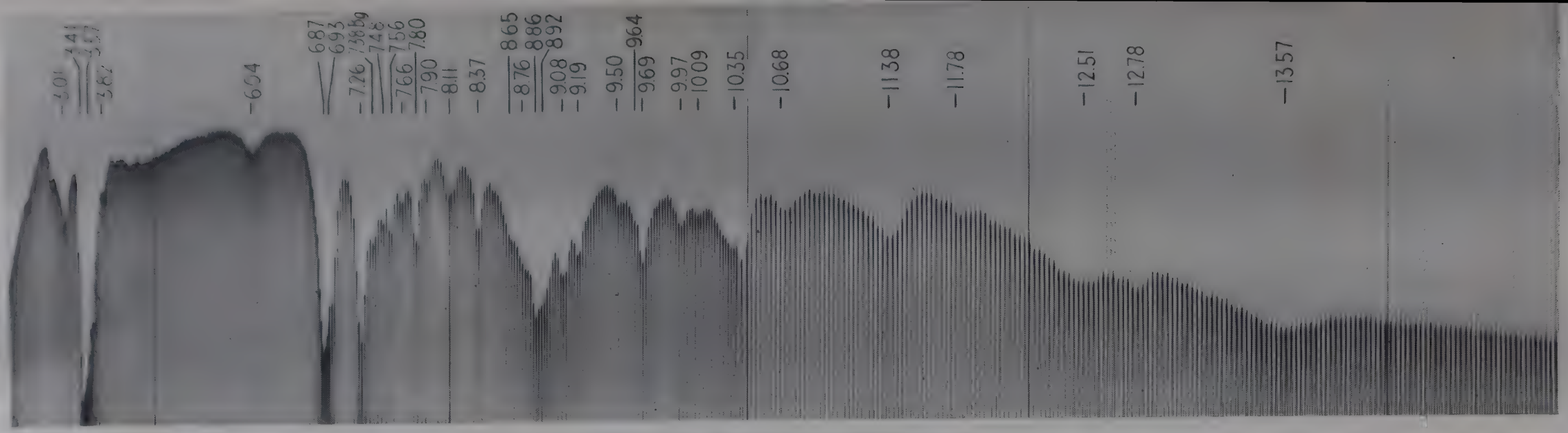


PLATE 311. Preparations: 0.015 mm.



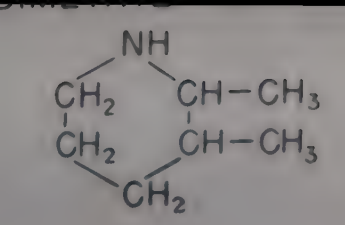
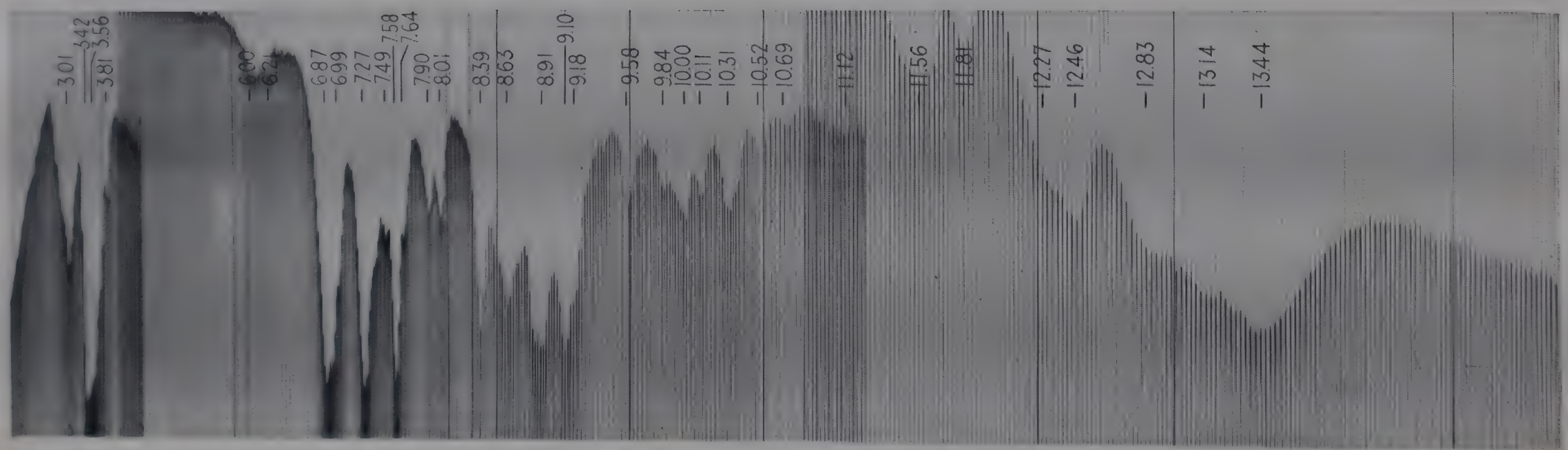


PLATE 312. Preparations: 0.015 mm.



2,4-DIMETHYLPIPERIDINE

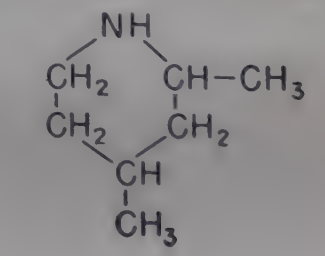


PLATE 313. Preparations: 0.015 mm.

BENZENE

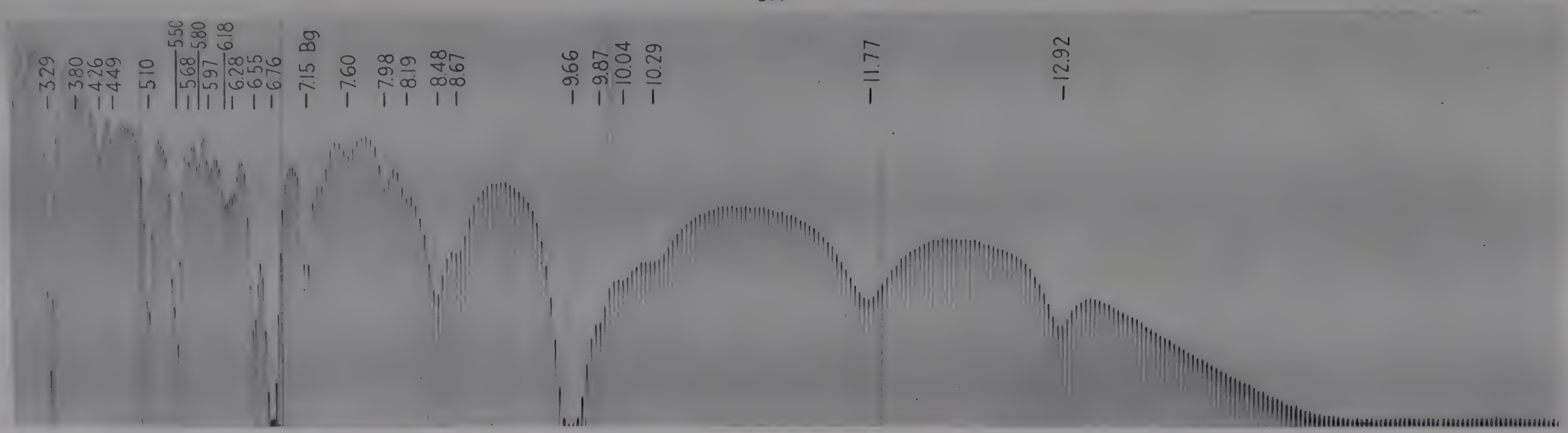


PLATE 314. Preparations: 0.10 mm.

PYRROLE

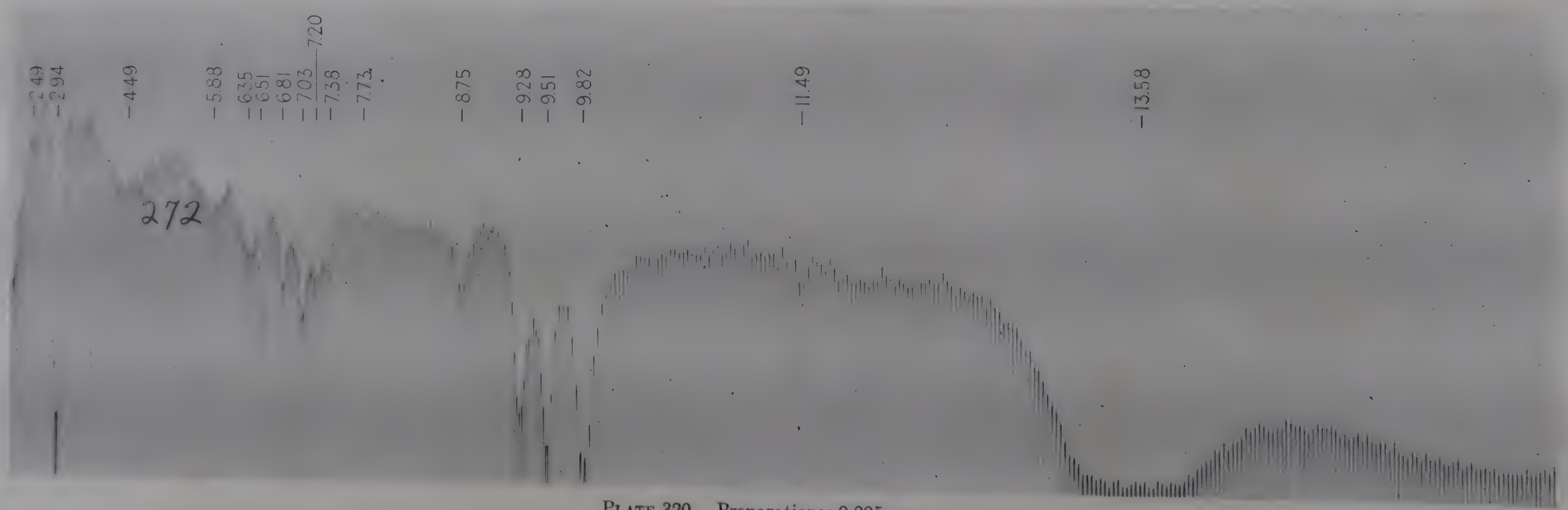


PLATE 320. Preparations: 0.005 mm.

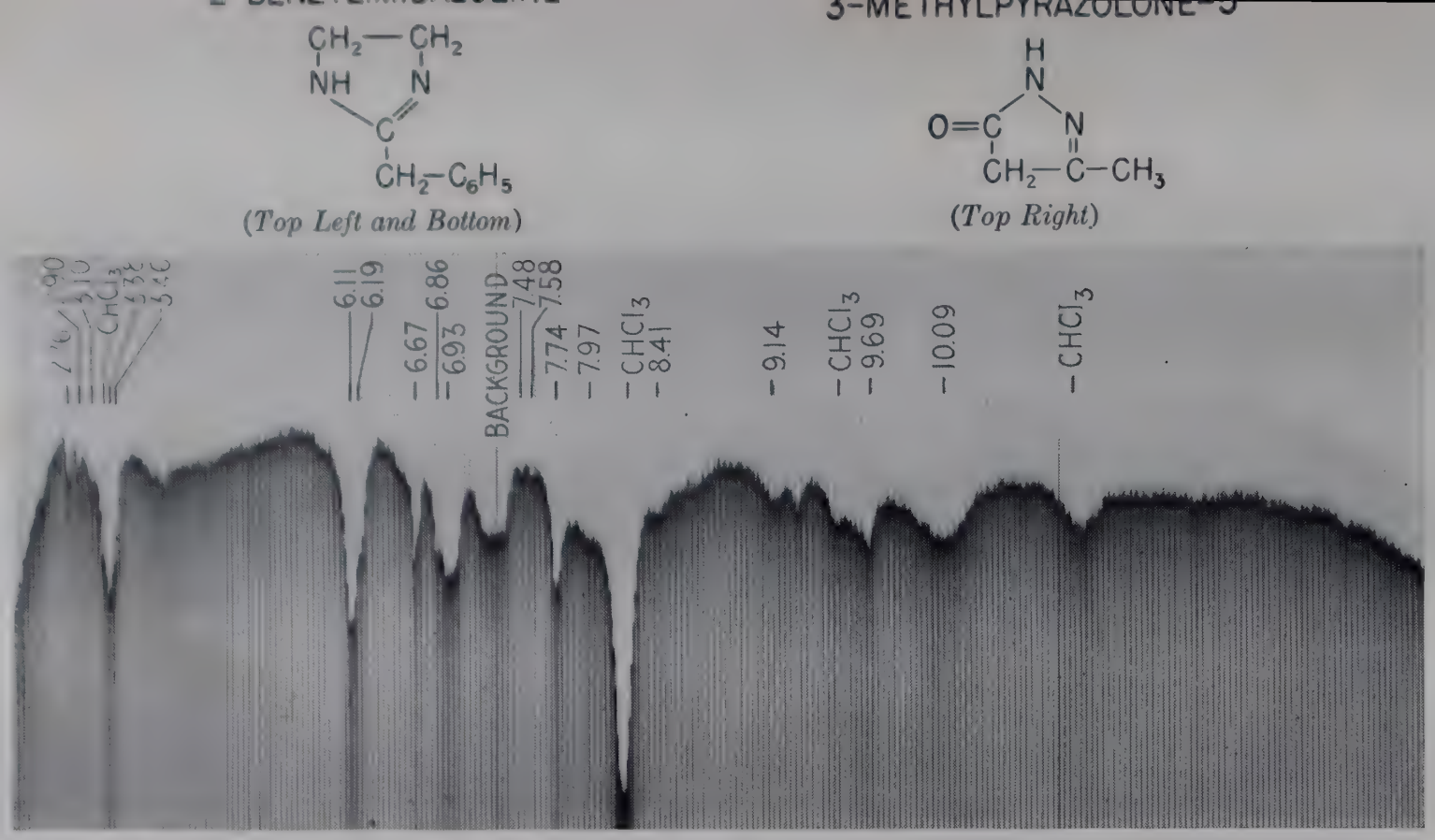


PLATE 319a. Assignments: 6.11 μ C=N; 6.19 μ, 6.67 μ Phenyl. Preparations: Saturated solution in $CHCl_3$, 0.015 mm.

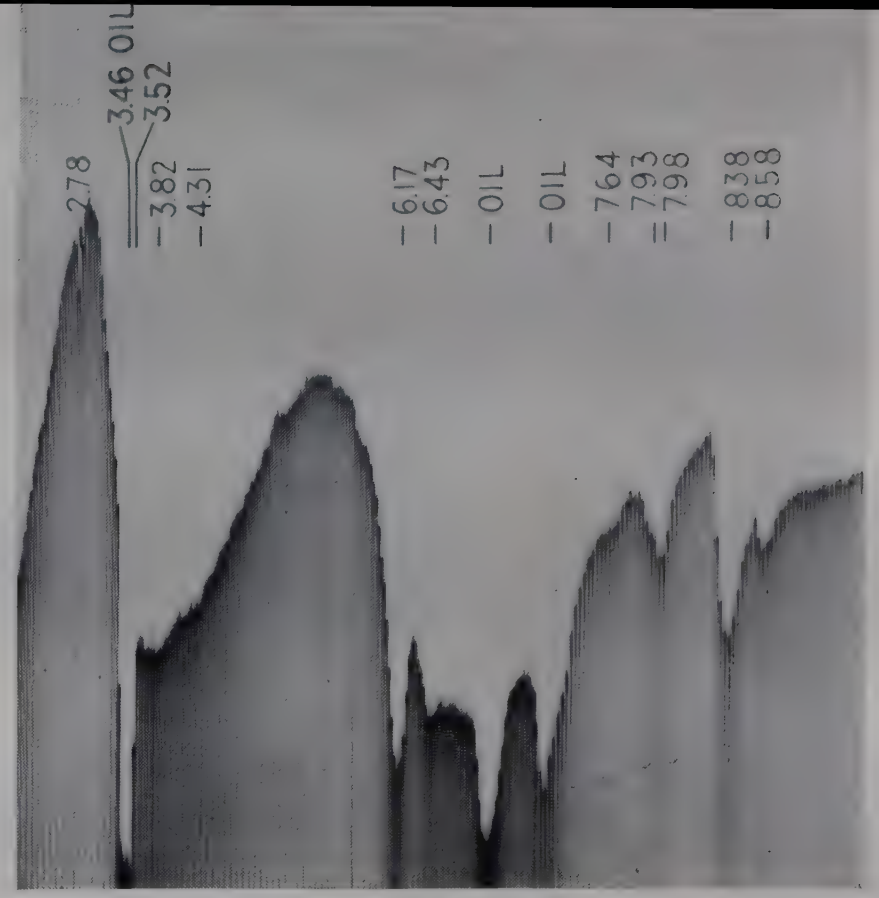


PLATE 315. Assignments: 6.17 μ C=N

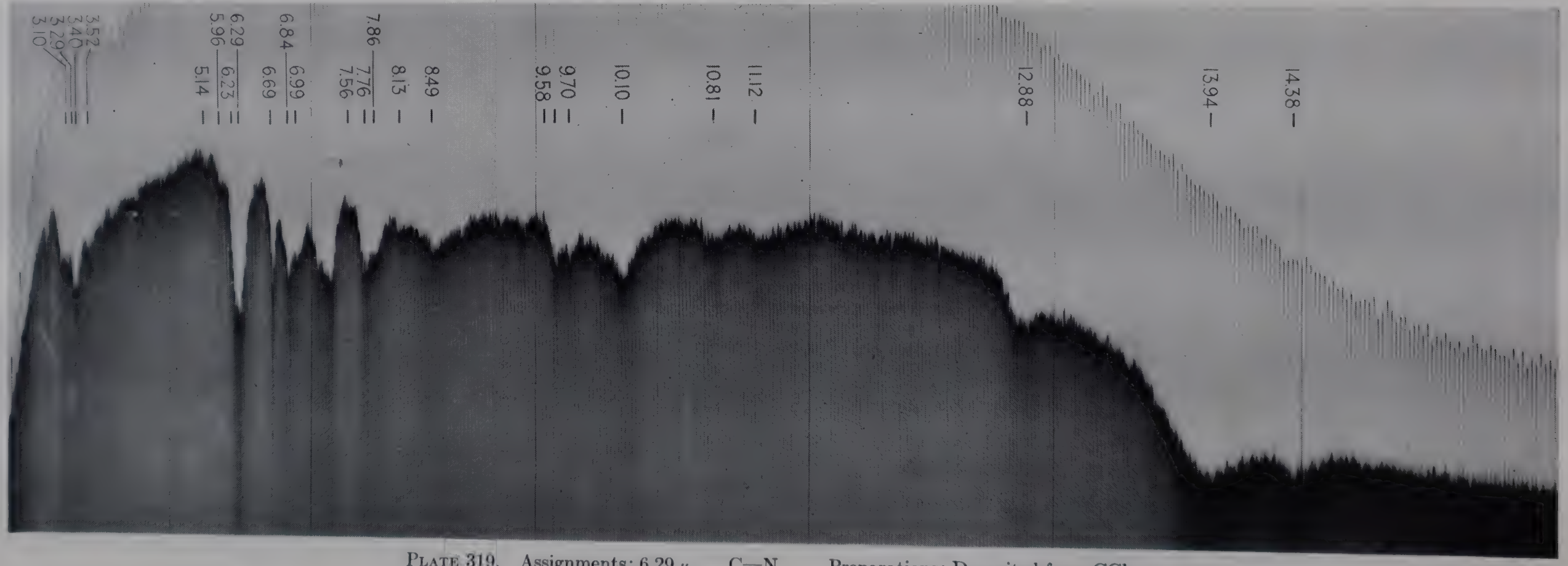


PLATE 319. Assignments: 6.29 μ C=N; 6.23 μ, 6.69 μ Phenyl. Preparations: Deposited from CCl_4

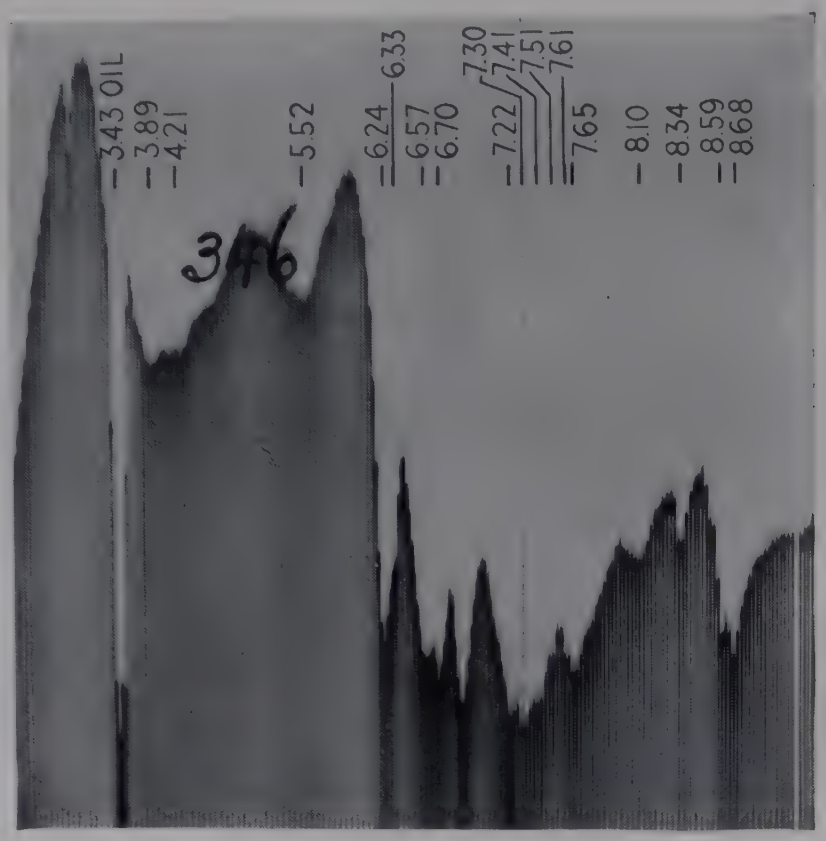
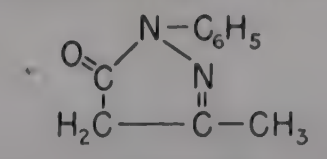


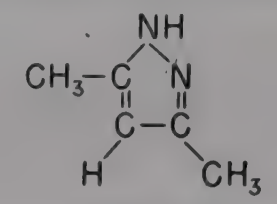
PLATE 316. Preparations: Oil paste

1-PHENYL-3-METHYL PYRAZOLONE-5



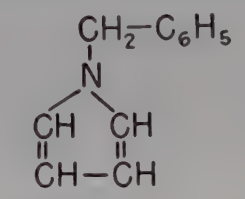
(Top Left)

3,5-DIMETHYLPYRAZOLE



(Top Right)

N-BENZYLPYRROLE



(Bottom)

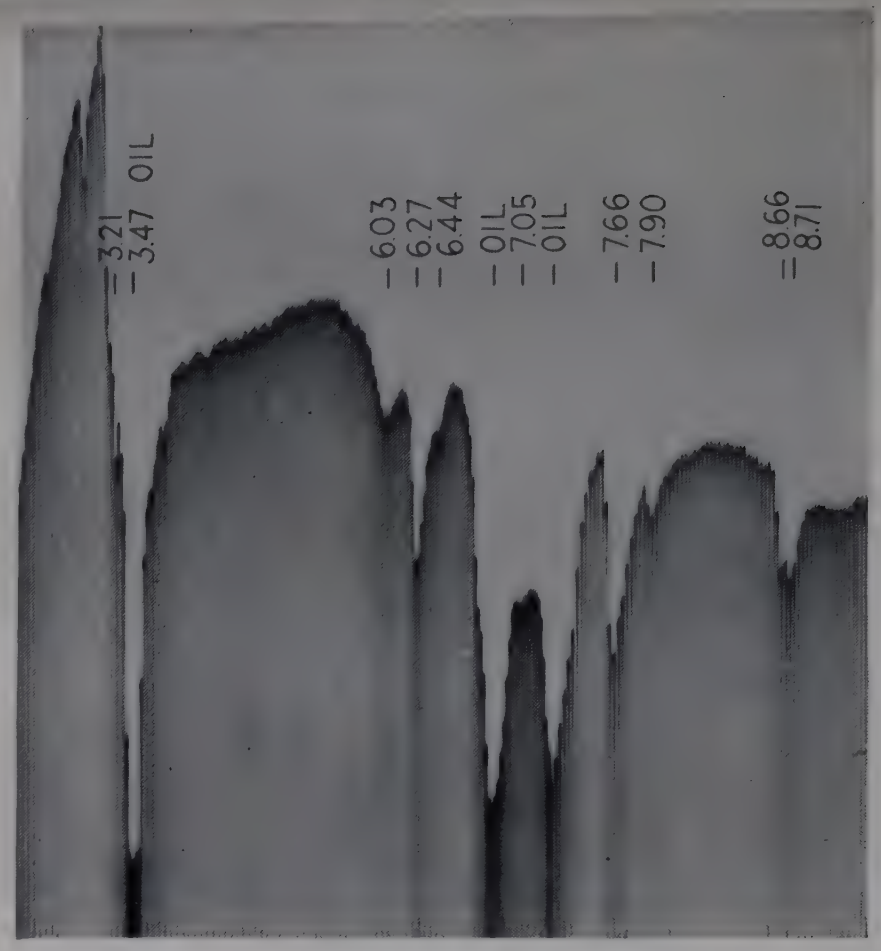


PLATE 317. Assignments: 6.03 μ C=C
6.27 μ C=N
Preparations: Oil paste

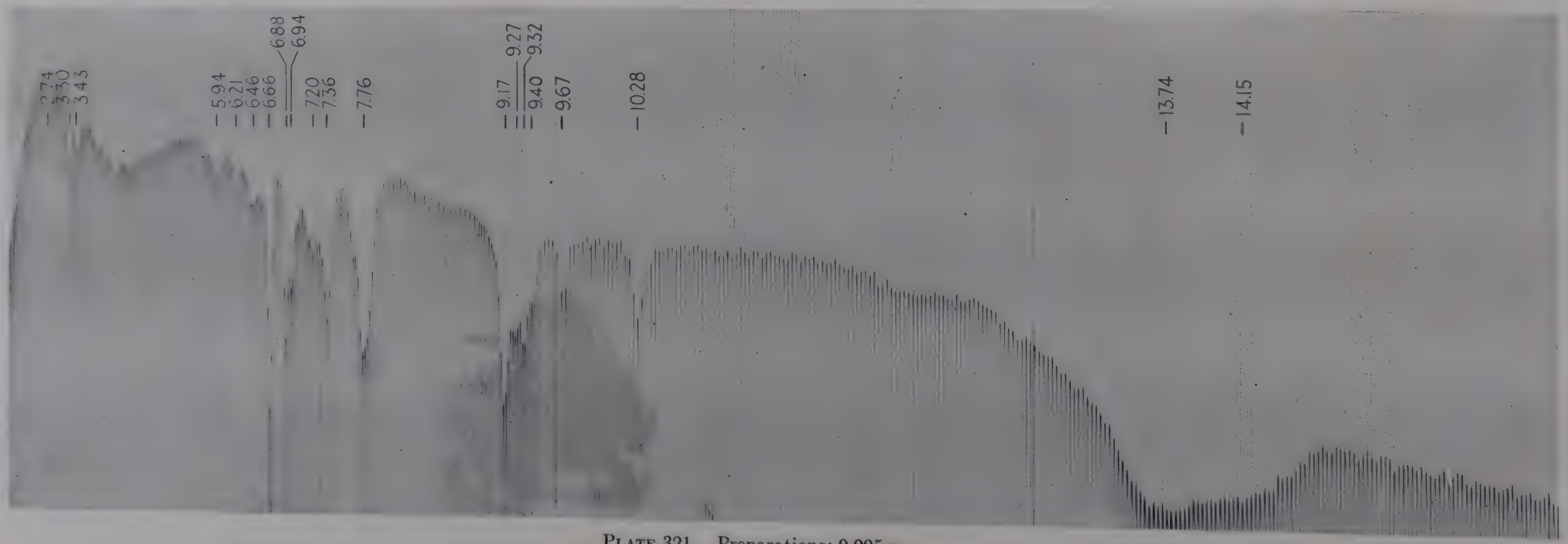
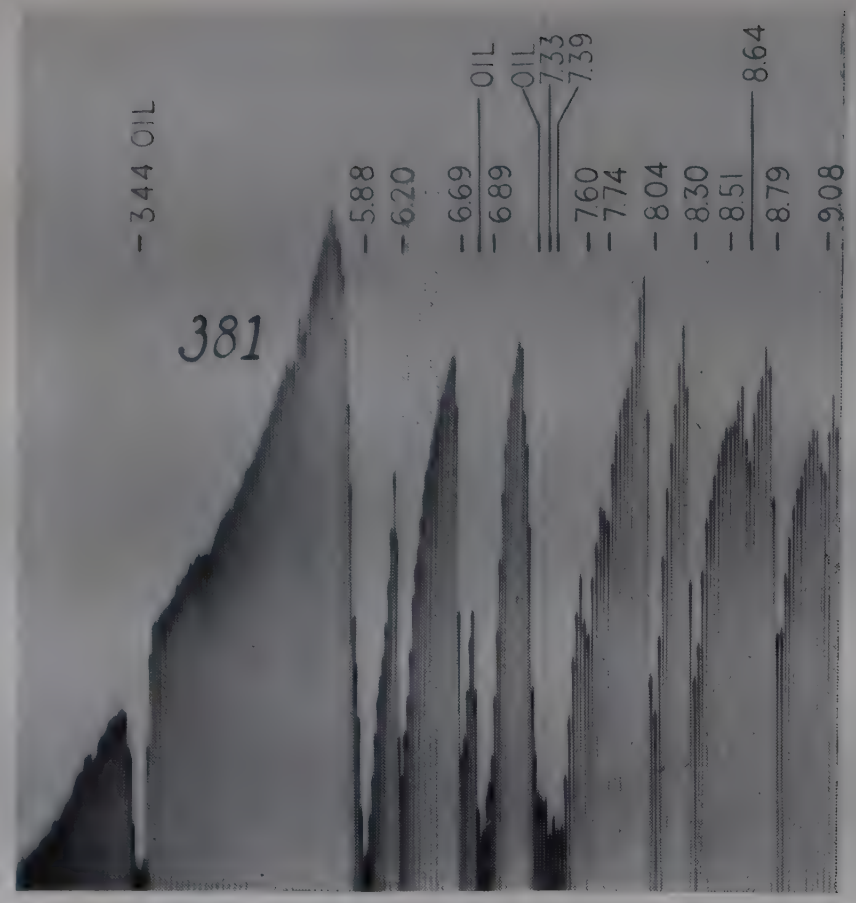


PLATE 321. Preparations: 0.005 mm.



1-ETHYLOXINDOLE-2

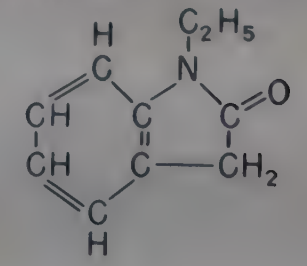
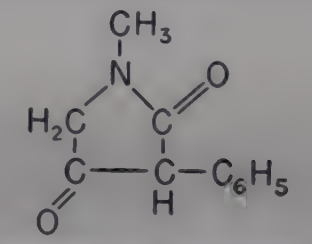


PLATE 318. Assignments: 5.88 μ C=O
6.20 μ, 6.69 μ } Ring
Preparations: Oil paste

1-METHYL-2,4-DIOXO-3-PHENYL-PYRROLIDINE



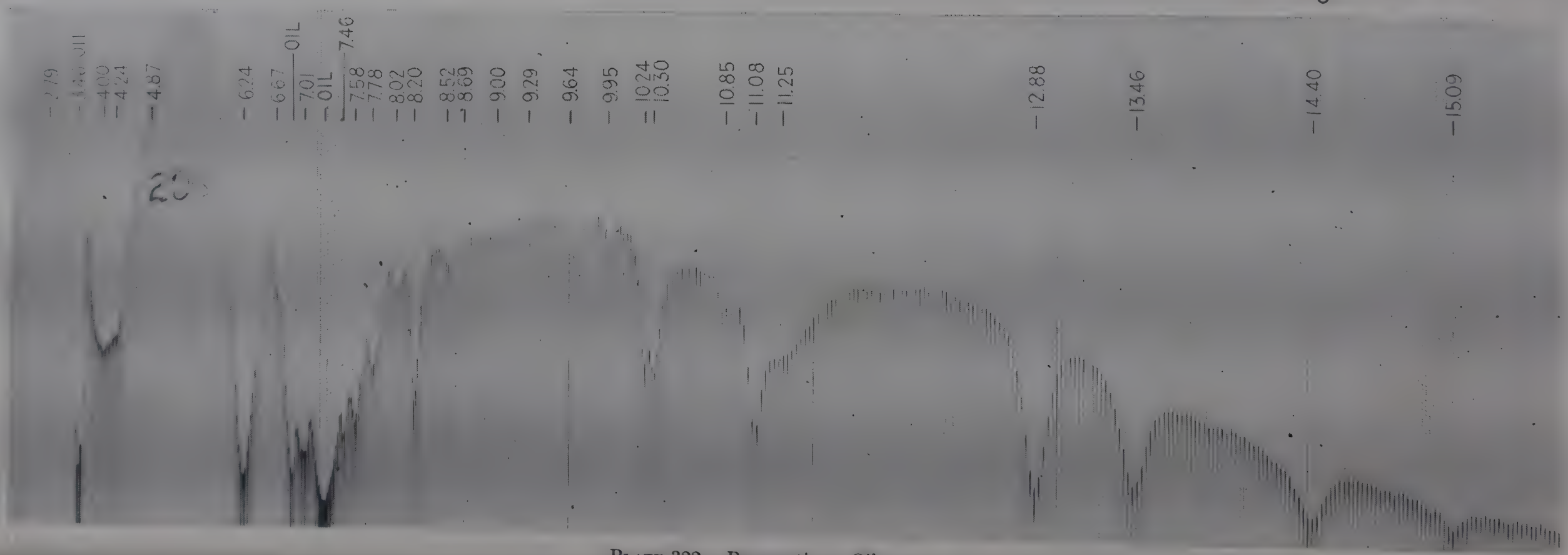
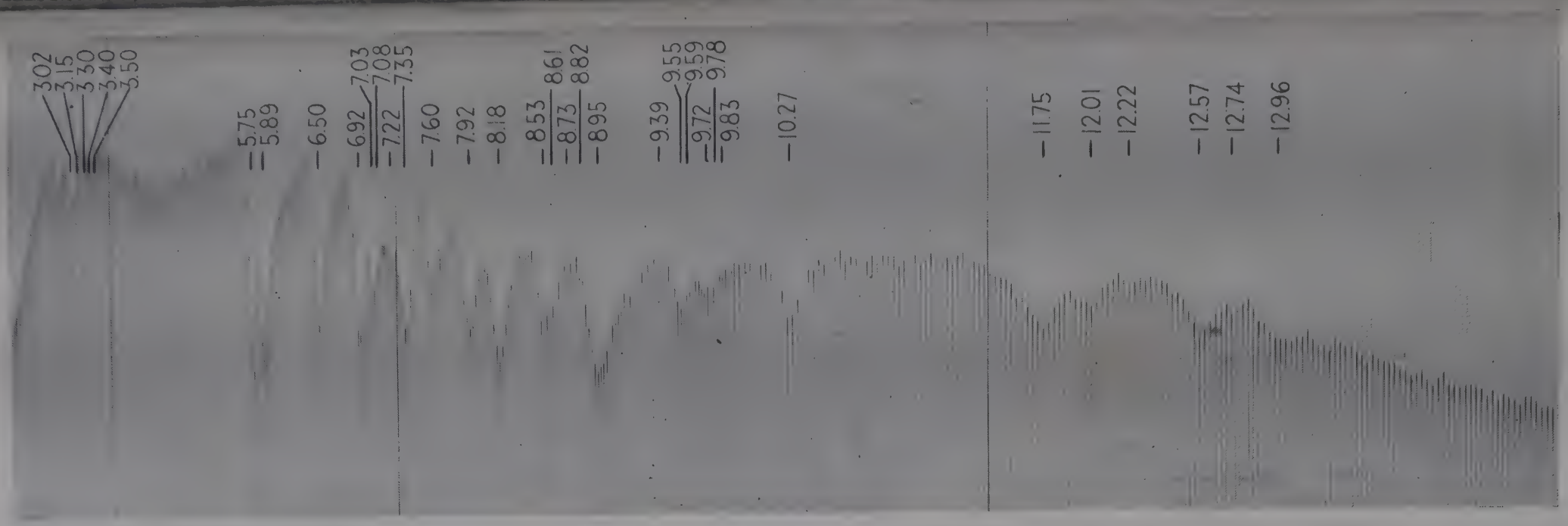


PLATE 322. Preparations: Oil paste



Δ^2-PYRAZOLINE-3,4-DICARBOXYLIC ACID DIMETHYL ESTER

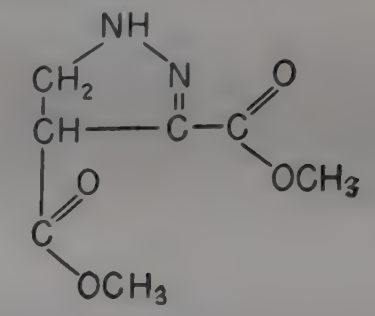
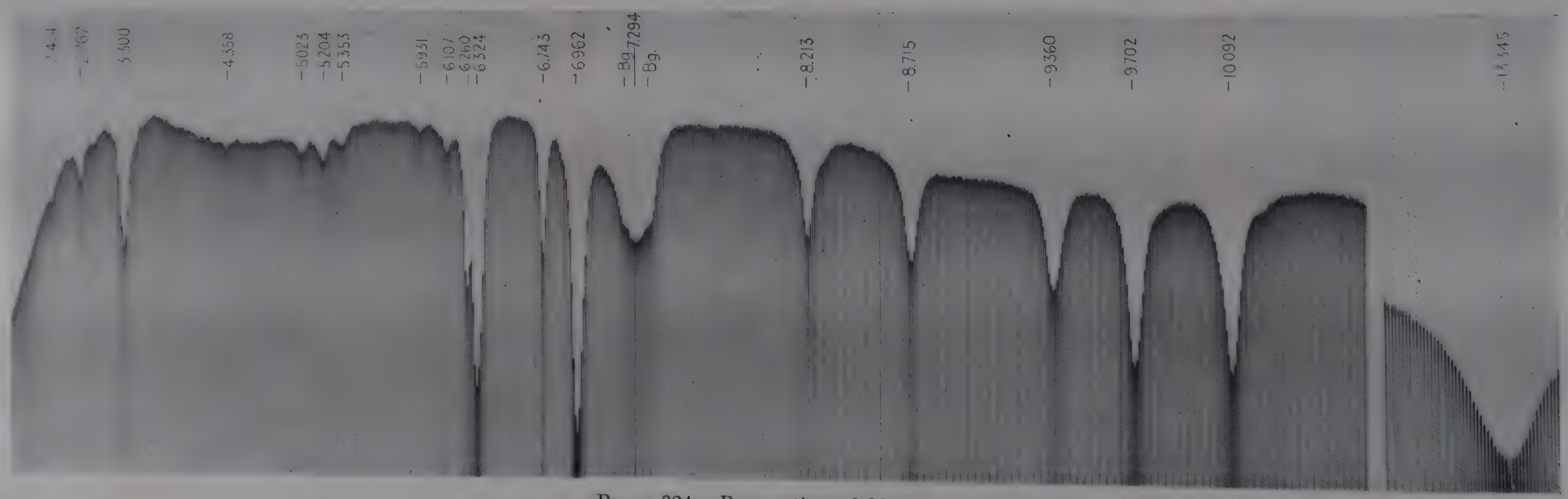


PLATE 323. Assignments: 5.75 μ Ester C=O (unconjugated moiety) Preparations: Deposited from $CHCl_3$
5.89 μ Ester C=O (conjugated)
6.50 μ C=N (conjugated)



PYRIDINE

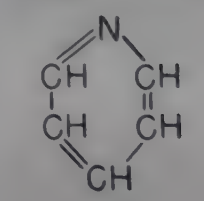


PLATE 324. Preparations: 0.01 mm.

dl-ALANINE HYDROCHLORIDE

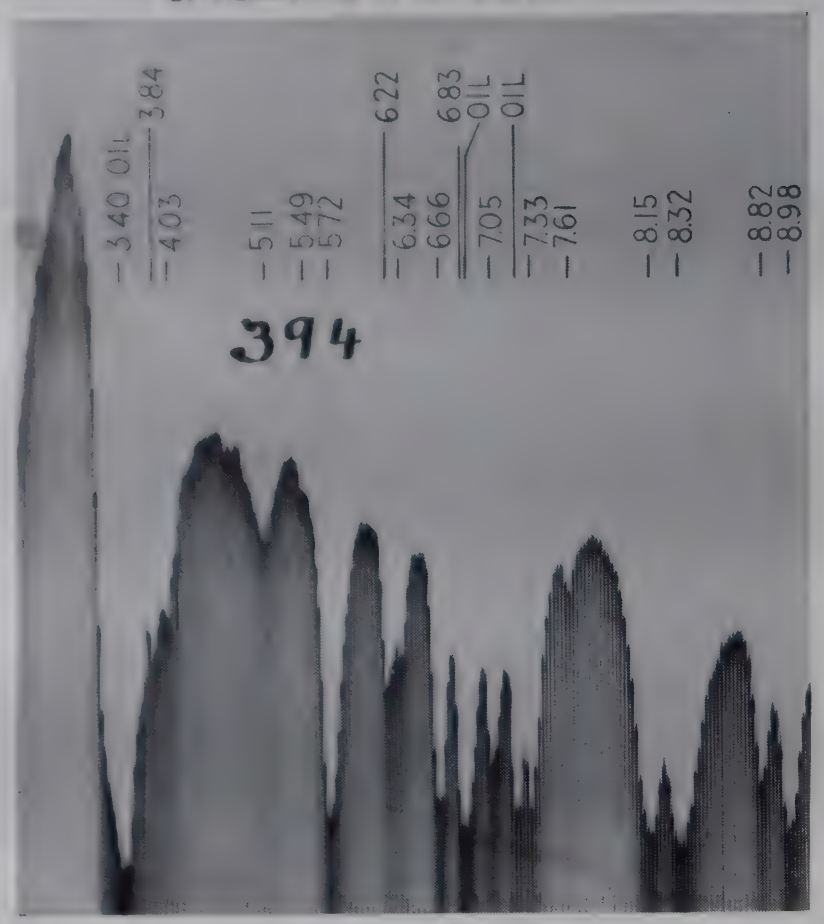


PLATE 326. Assignments:

5.72 μ	Acid C=O
6.22 μ	δNH_3^+
6.34 μ	Unassigned
6.66 μ	Amino acid hydrochloride II

Preparations: Oil paste

dl-α-AMINO-α-METHYLBUTYRIC ACID HYDROCHLORIDE

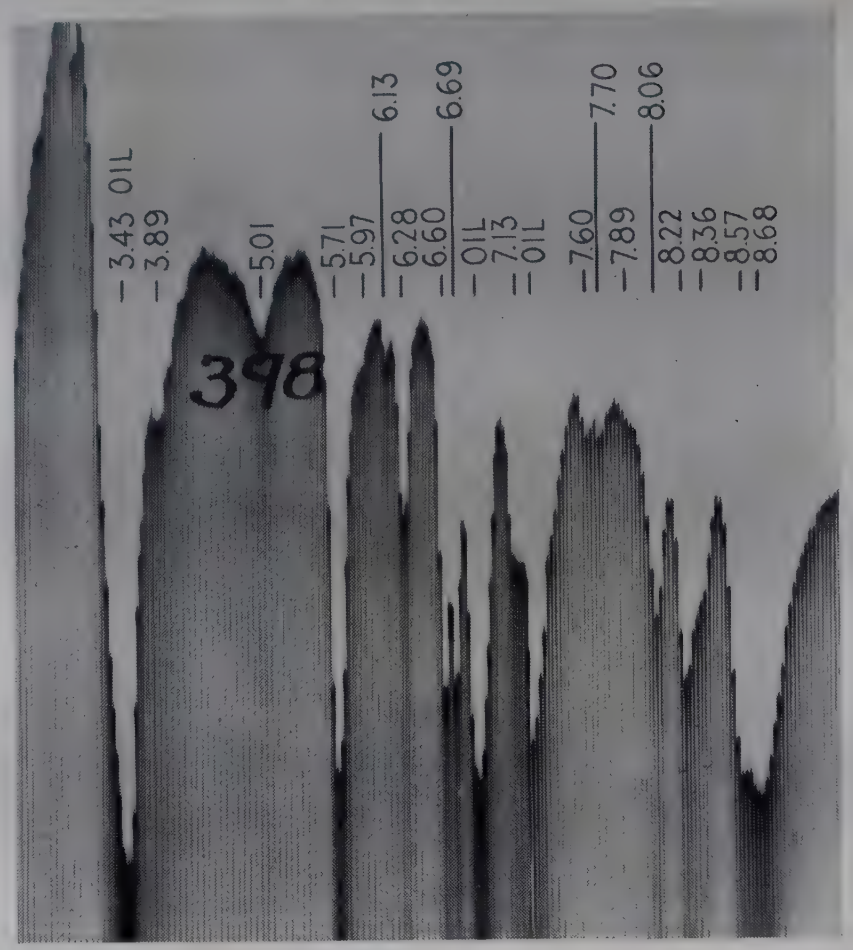


PLATE 328. Assignments:

5.71 μ	Acid C=O
6.28 μ	δNH_3^+
6.60 μ, 6.69 μ	Amino acid hydrochloride II

Preparations: Oil paste

α-AMINOISOBUTYRIC ACID HYDROCHLORIDE

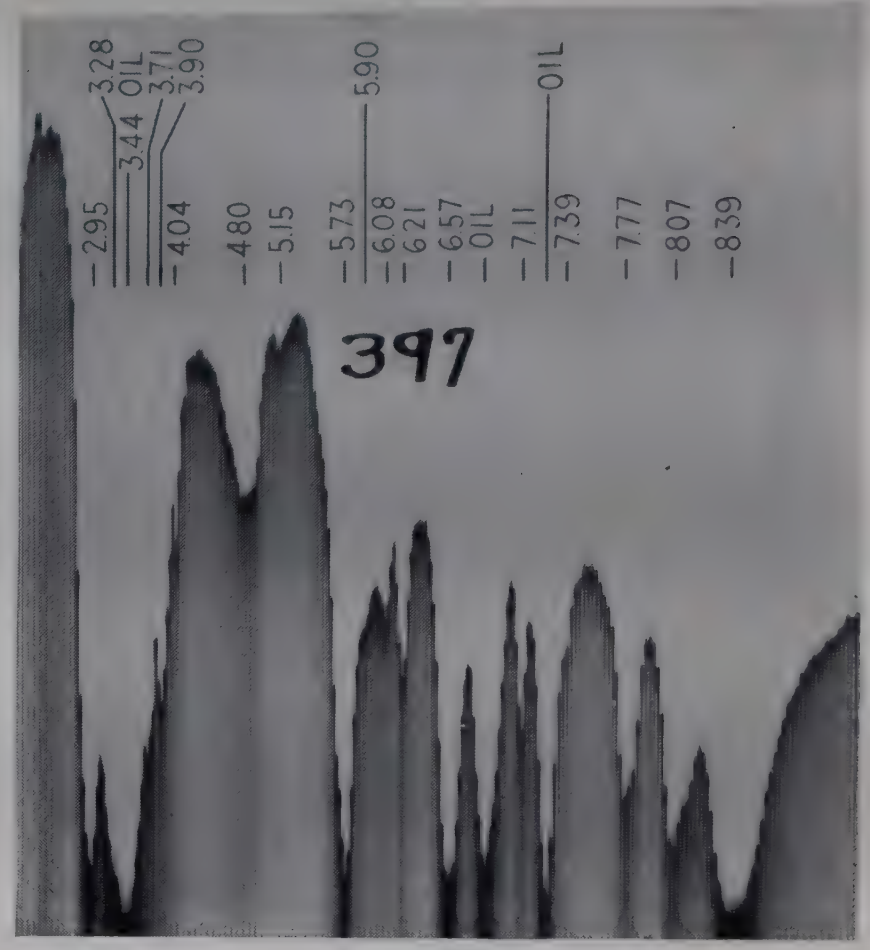
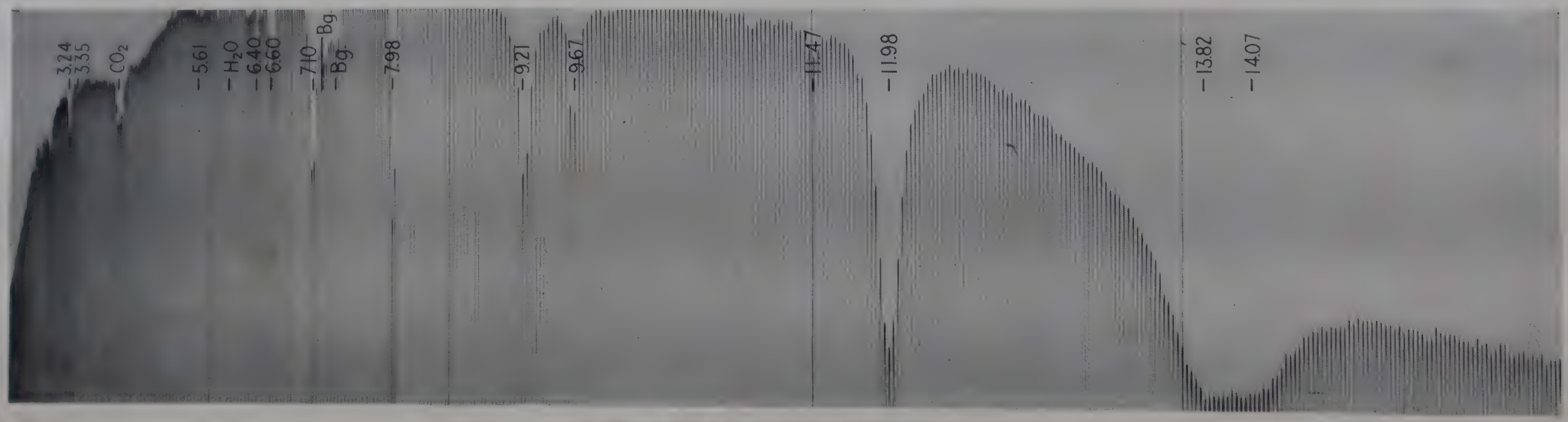


PLATE 327. Assignments:

5.73 μ	Acid C=O
6.21 μ	δNH_3^+
6.57 μ	Amino acid hydrochloride II

Preparations: Oil paste



THIOPHENE

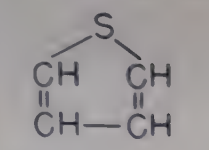


PLATE 325. Preparations: 0.005 mm.

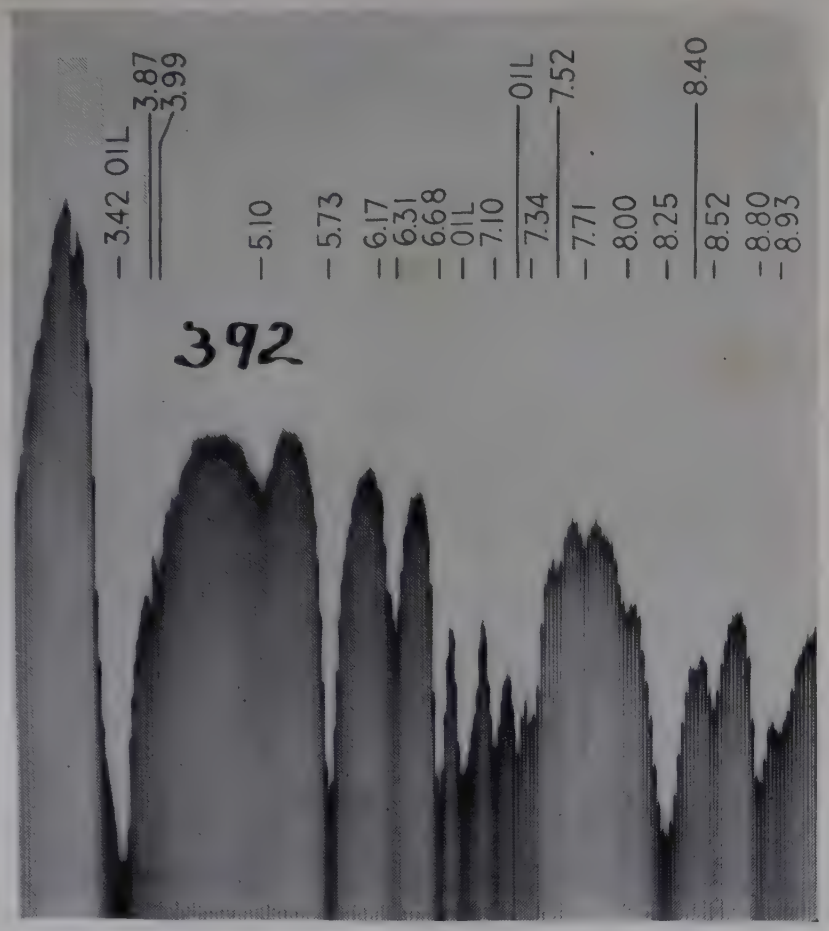


PLATE 329. 5.73 μ Acid C=O; 6.31 μ δNH_3^+; 6.68 μ Amino acid hydrochloride II. Oil paste

dl-α-AMINO-n-VALERIC ACID HYDROCHLORIDE
(Top Left)

dl-α-AMINO-n-CAPROIC ACID HYDROCHLORIDE
(Top Right)

L-GLUTAMIC ACID HYDROCHLORIDE

$$HO_2C-(CH_2)_2-\underset{\displaystyle NH_3^+Cl^-}{\underset{|}{CH}}-CO_2H$$

(Bottom Left)

CYSTINE HYDROCHLORIDE

$$[-S-CH_2-CH(NH_2)CO_2H]_2 \cdot 2HCl$$

(Bottom Center)

CYSTEINE HYDROCHLORIDE

$$HS-CH_2-\underset{\displaystyle NH_3^+Cl^-}{\underset{|}{CH}}-CO_2H$$

(Bottom Right)

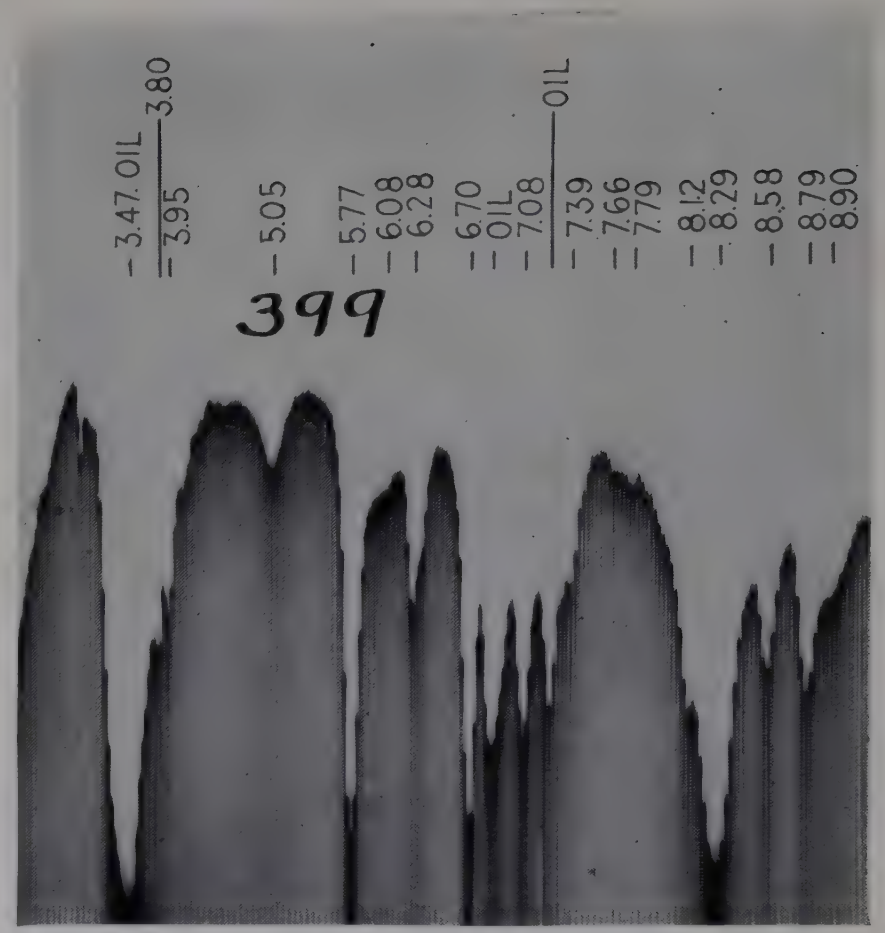


PLATE 330. 5.77 μ Acid C=O; 6.28 μ δNH_3^+; 6.70 μ Amino acid hydrochloride II. Oil paste

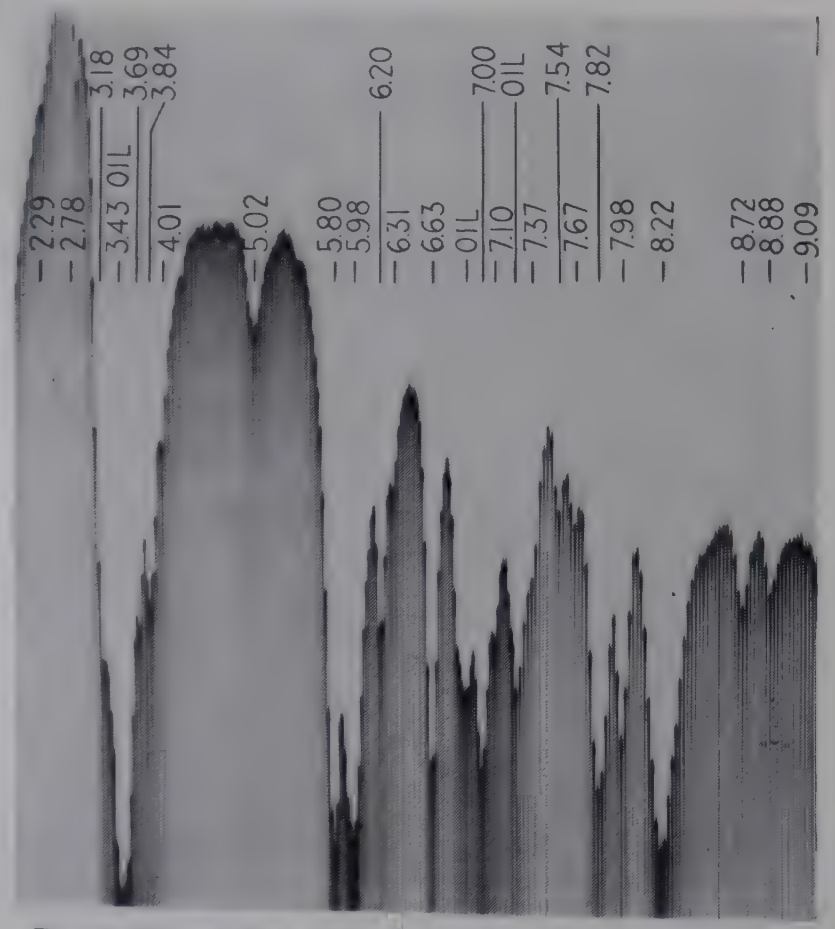


PLATE 331. 5.80 μ, 5.98 μ Acid C=O; 6.20 μ δNH_3^+; 6.63 μ Amino acid hydrochloride II. Oil paste

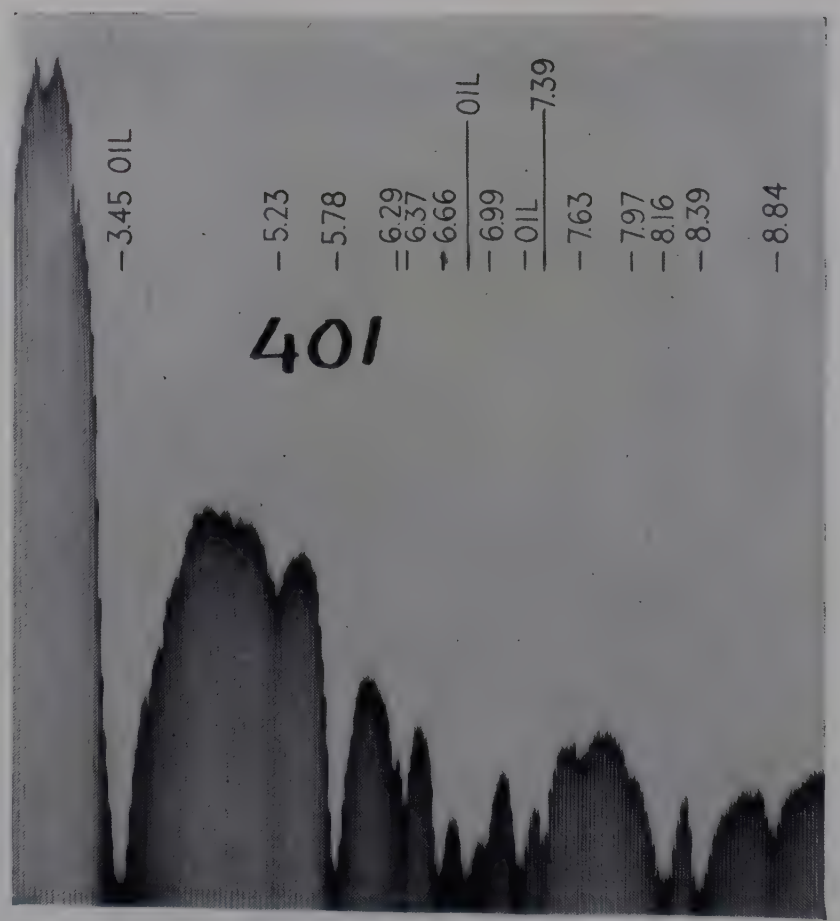


PLATE 332. 5.78 μ Acid C=O; 6.29 μ, 6.37 μ δNH_3^+; 6.66 μ Amino acid hydrochloride II. Oil paste

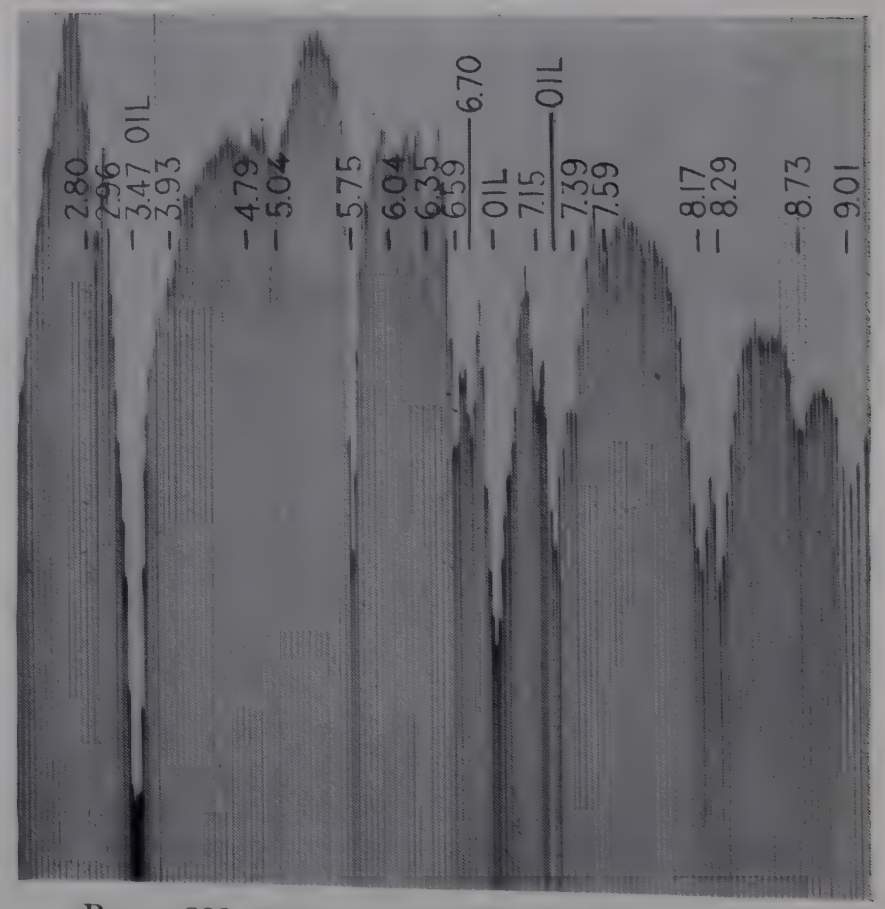


PLATE 333. 5.75 μ Acid C=O; 6.35 μ δNH_3^+;

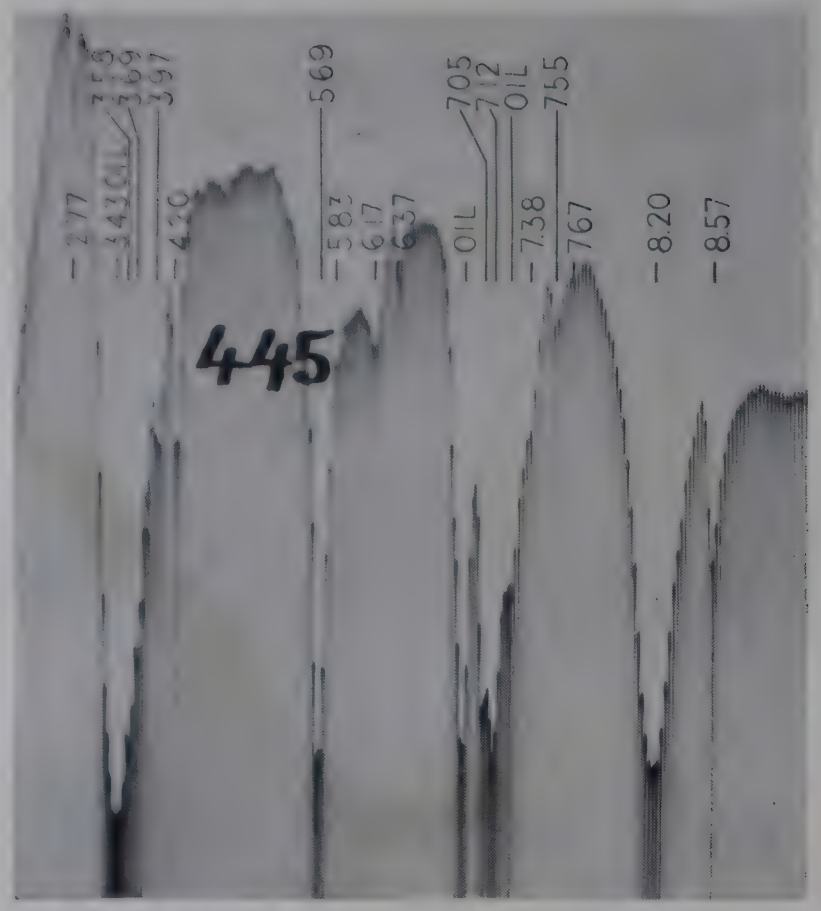


PLATE 334. Assignments: 5.69 μ Acid C=O
Preparations: Oil paste

SARCOSINE HYDROCHLORIDE
$[CH_3-NH_2-CH_2-CO_2H]^+Cl^-$
(Top Left)

N-PHENYLGLYCINE HYDROCHLORIDE
(Top Right)

dl-β-PHENYLALANINE HYDROCHLORIDE
(Bottom Left)

δ-AMINO-n-VALERIC ACID
HYDROCHLORIDE
$H_3^+N-CH_2-(CH_2)_3-CO_2H$
Cl^-
(Bottom Center)

l-PROLINE HYDROCHLORIDE
(Bottom Right)

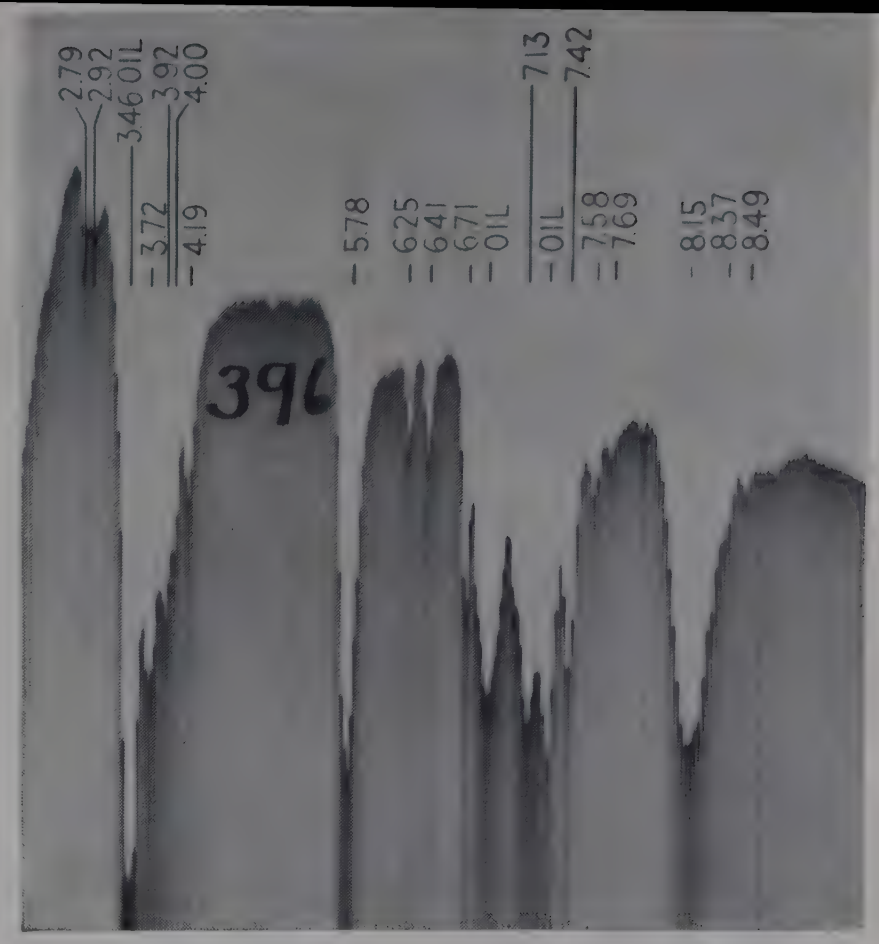


PLATE 335. 5.78 μ Acid C=O;
6.25 μ, 6.41 μ, 6.71 μ Anilino. Oil paste

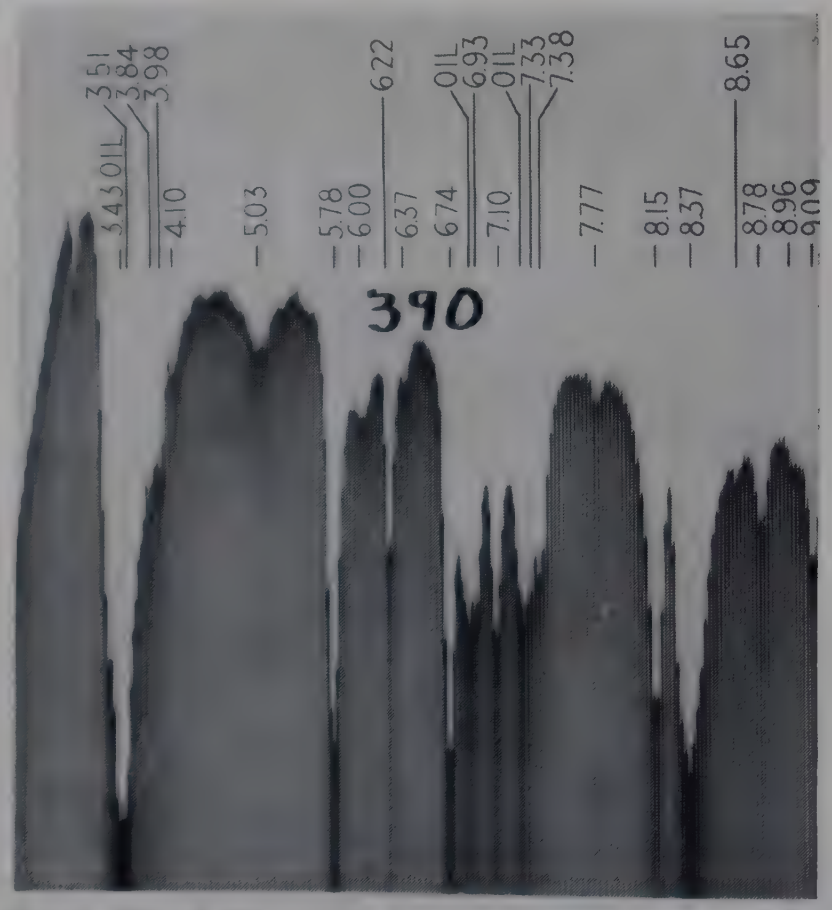


PLATE 336. 5.78 μ Acid C=O; 6.22 μ δNH_3^+, phenyl;
6.74 μ Amino acid hydrochloride II, phenyl. Oil paste

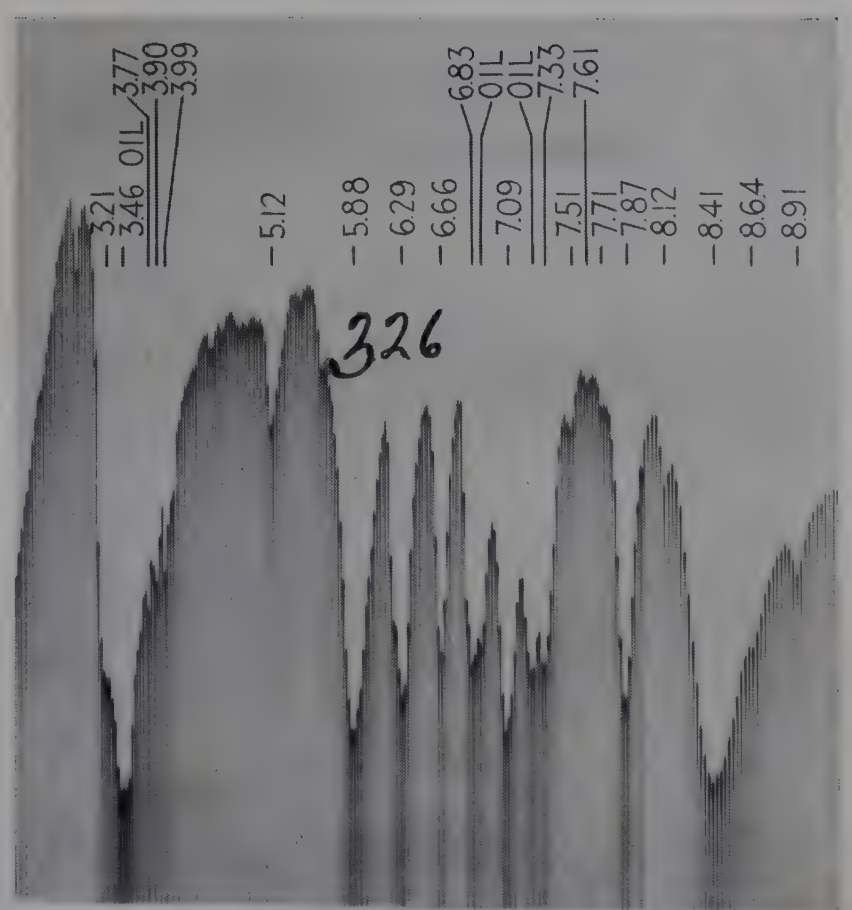


PLATE 337. 5.88 μ Acid C=O; 6.29 μ δNH_3^+;
6.66 μ Amino acid hydrochloride II. Oil paste

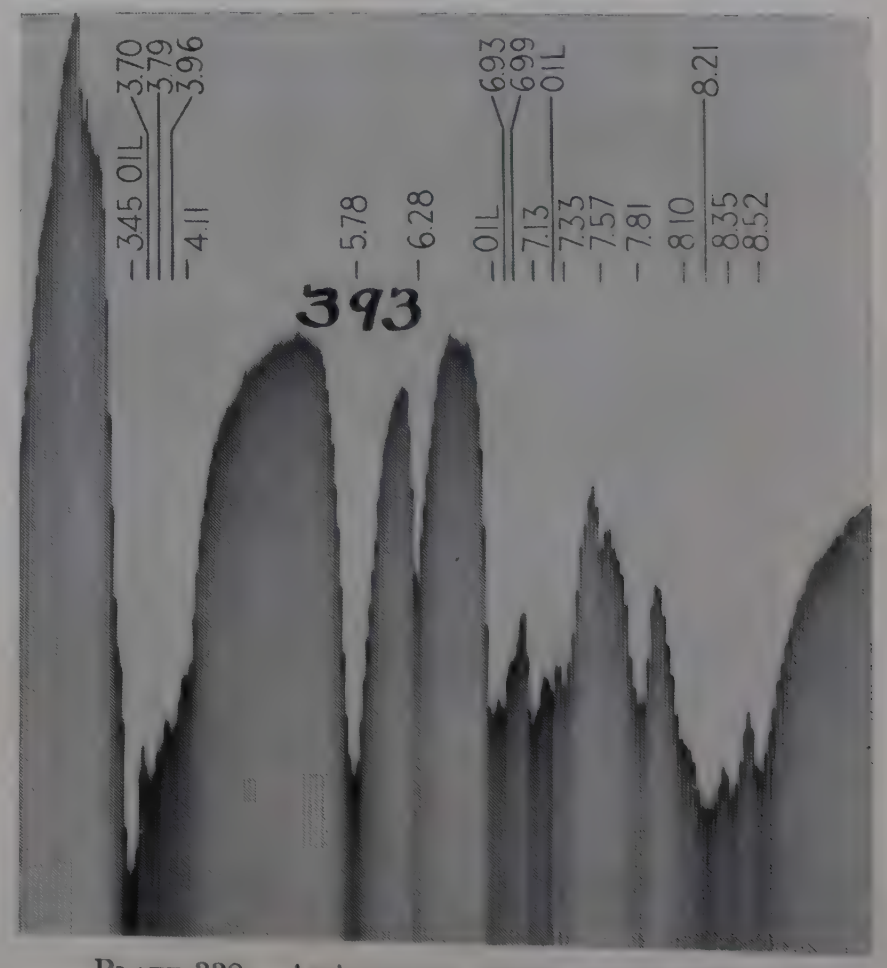


PLATE 338. Assignments: 5.78 μ Acid C=O
6.28 μ δNH_2^+
Preparations: Oil paste

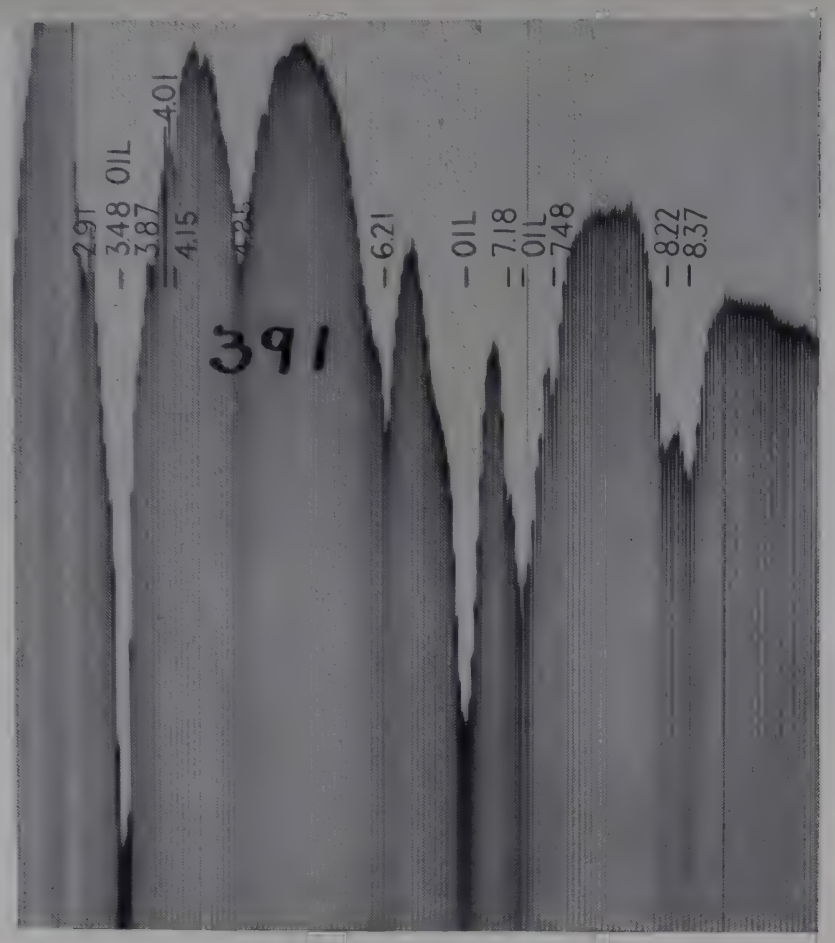


PLATE 339. Assignments: 6.21 μ δNH_3^+
Preparations: Oil paste

ETHYLAMINE HYDROCHLORIDE

$C_2H_5-\overset{+}{N}H_3\ Cl^-$

(Top Left)

I-TYROSINE HYDROCHLORIDE

(Top Right)

CREATININE HYDROCHLORIDE

(Bottom Left)

BENZYL CHLORIDE

$C_6H_5-CH_2-Cl$

(Bottom Right)

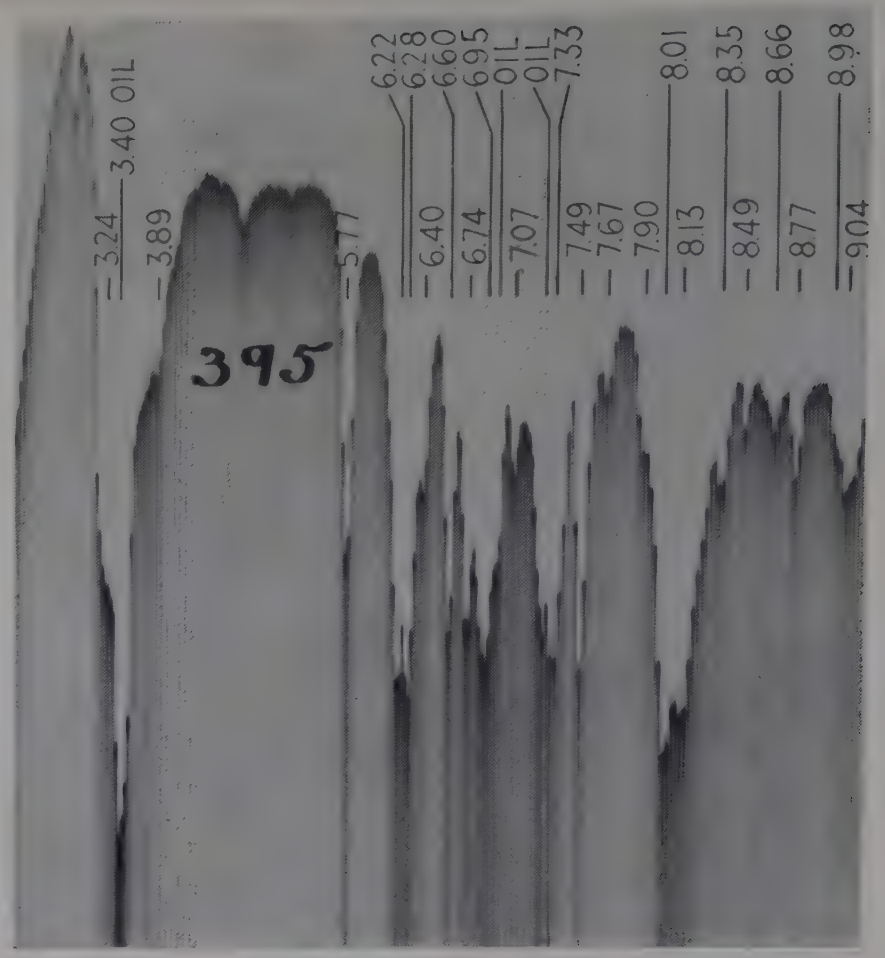


PLATE 340. Assignments:

5.77 μ	Acid C═O
6.22 μ	Phenyl
6.28 μ	δNH_3, phenyl
6.60 μ	Amino acid hydrochloride II
6.74 μ	Phenyl

Preparations: Oil paste

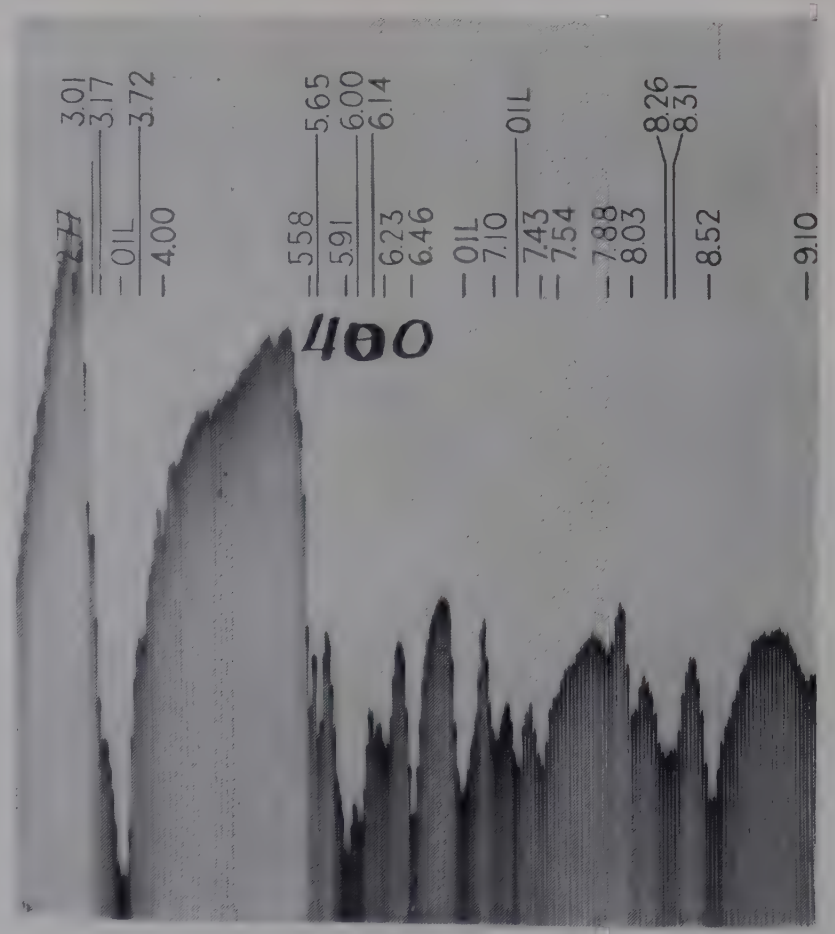


PLATE 341. Preparations: Oil paste

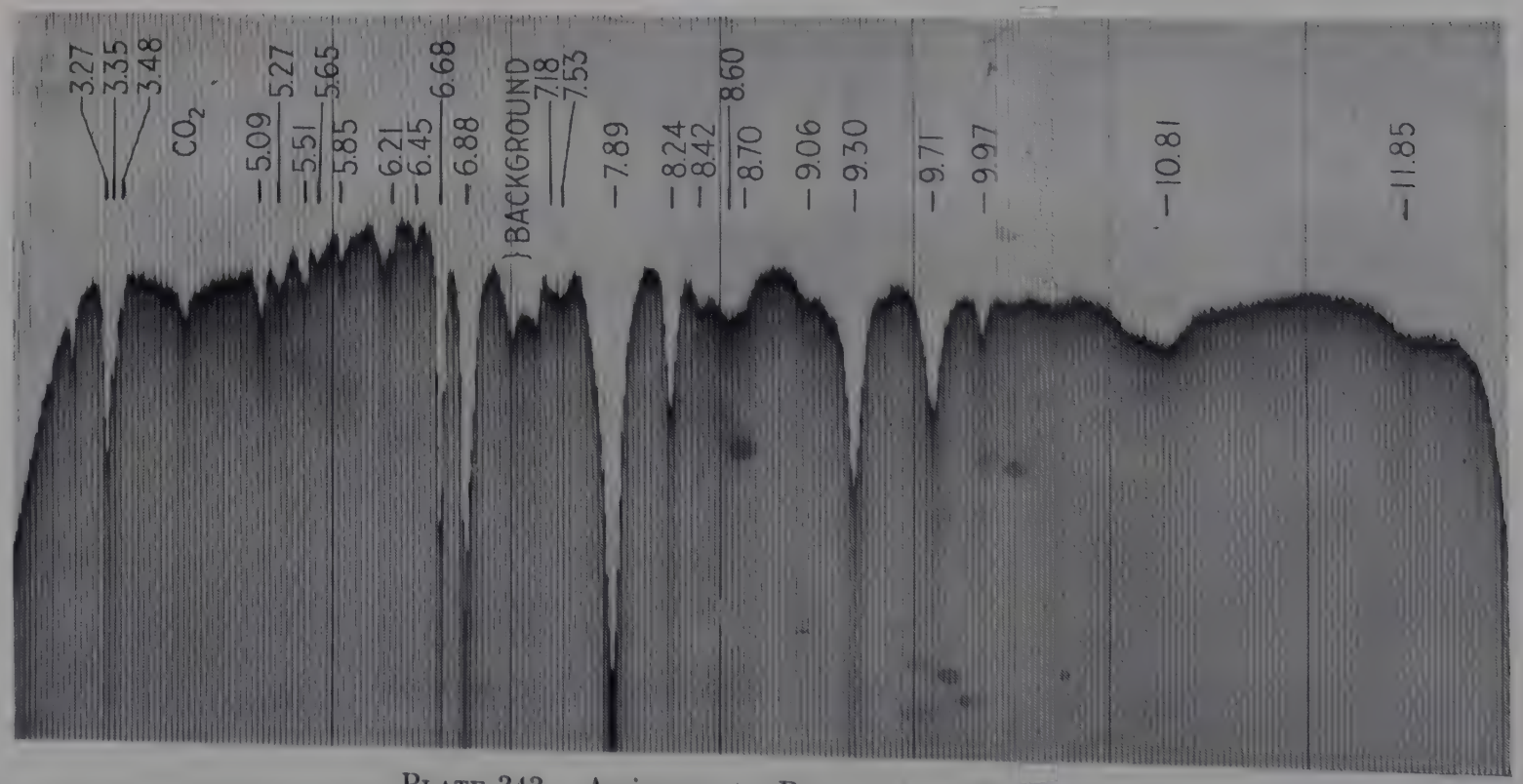
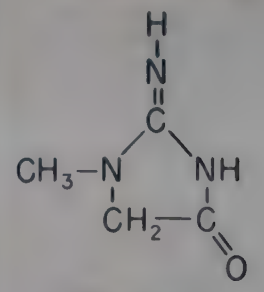


PLATE 343. Assignments: Preparations: 0.015

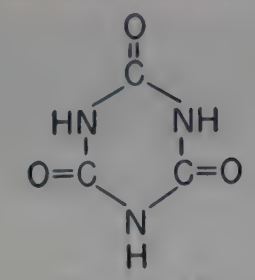
PLATE 342. Assignments: 5.99 μ 4-C=O
6.67 μ Amide II
Preparations: Oil paste

CREATININE



(*Top Left*)

CYANURIC ACID



(*Top Right*)

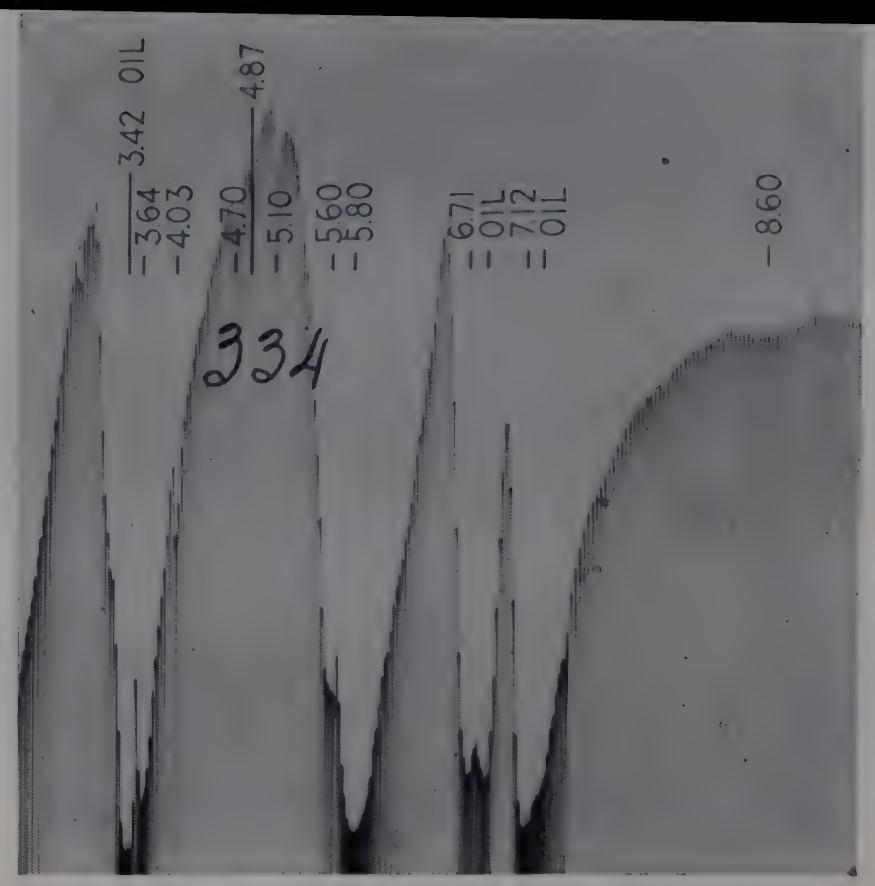


PLATE 344. Preparations: Oil paste

TRIETHYLAMINE OXIDE DIHYDRATE

$(C_2H_5)_3 -N=O \cdot 2H_2O$

(*Bottom*)

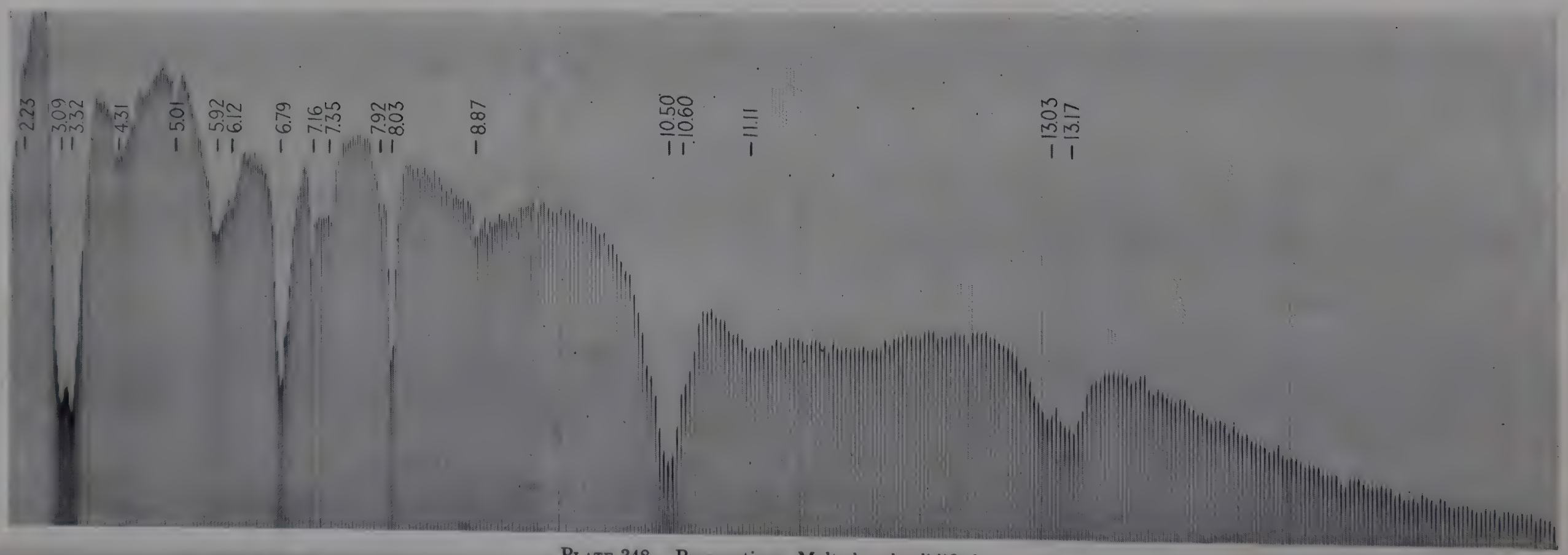


PLATE 348. Preparations: Melted and solidified

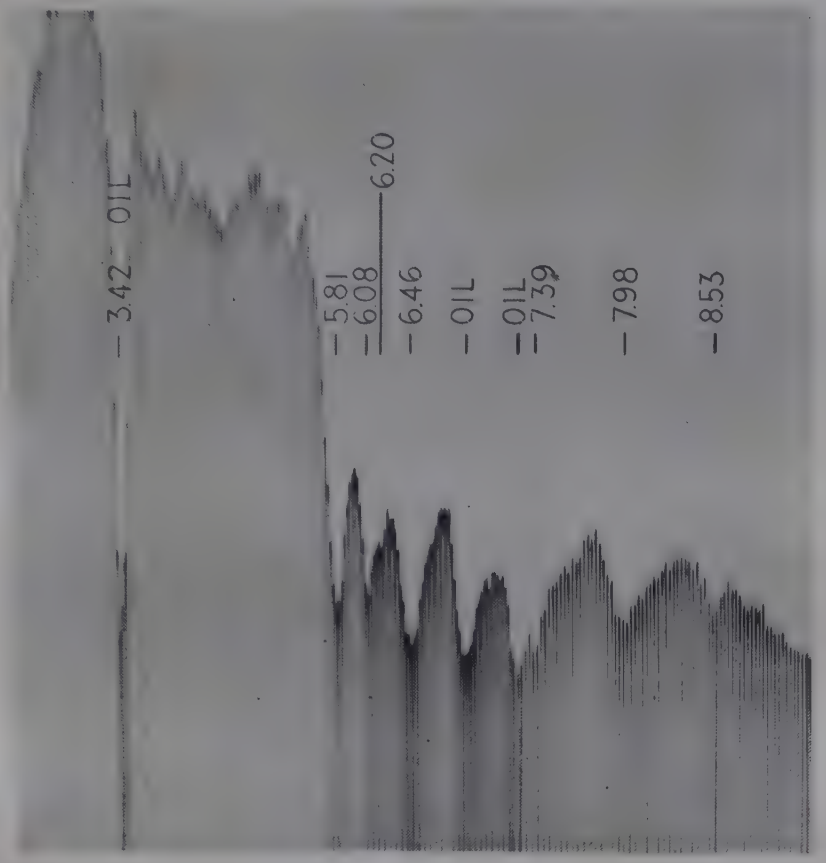
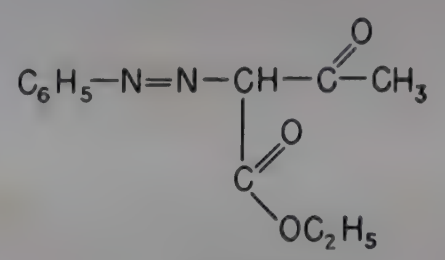


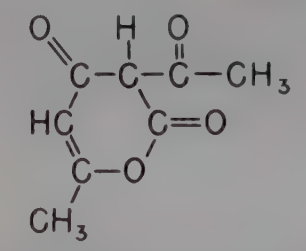
PLATE 346. Assignments: 5.81 μ Lactone C=O
Preparations: Oil paste

α-PHENYLAZOACETOACETIC ACID
ETHYL ESTER



(Top Right)

DEHYDRACETIC ACID



(Top Left and Bottom)

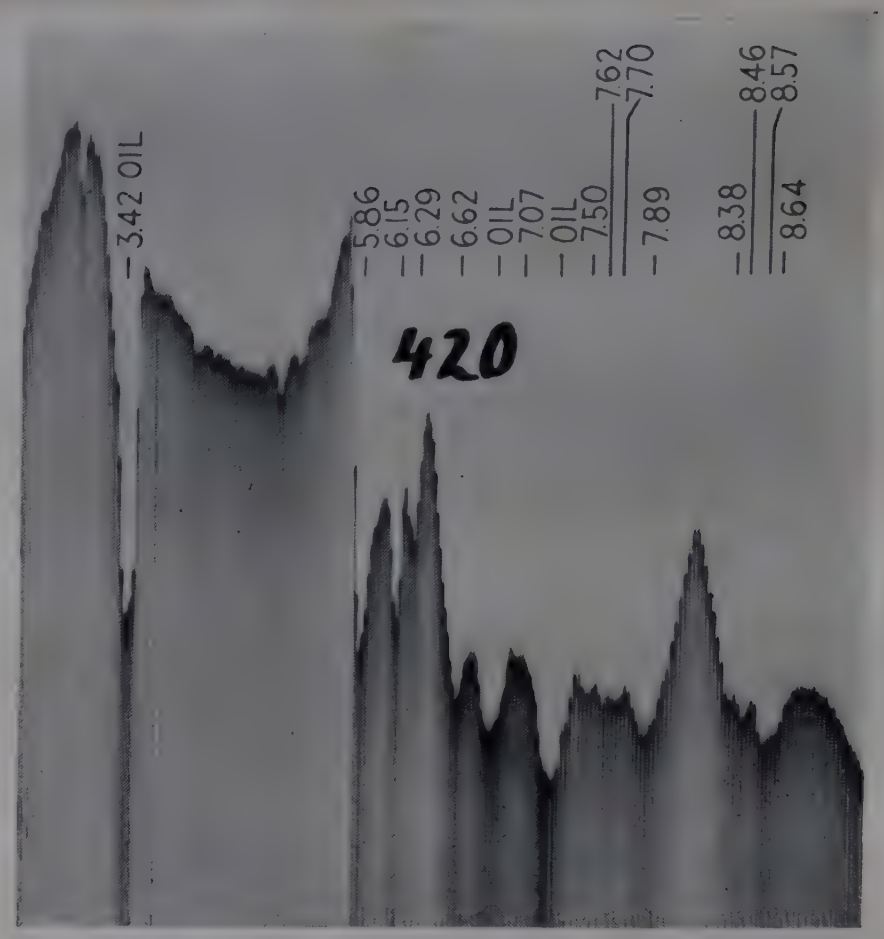


PLATE 345. Assignments:
5.86 μ Keto C=O, Ester C=O
6.15 μ N=N
6.29 μ Phenyl
6.62 μ C=C (enol)
Preparations: Oil paste

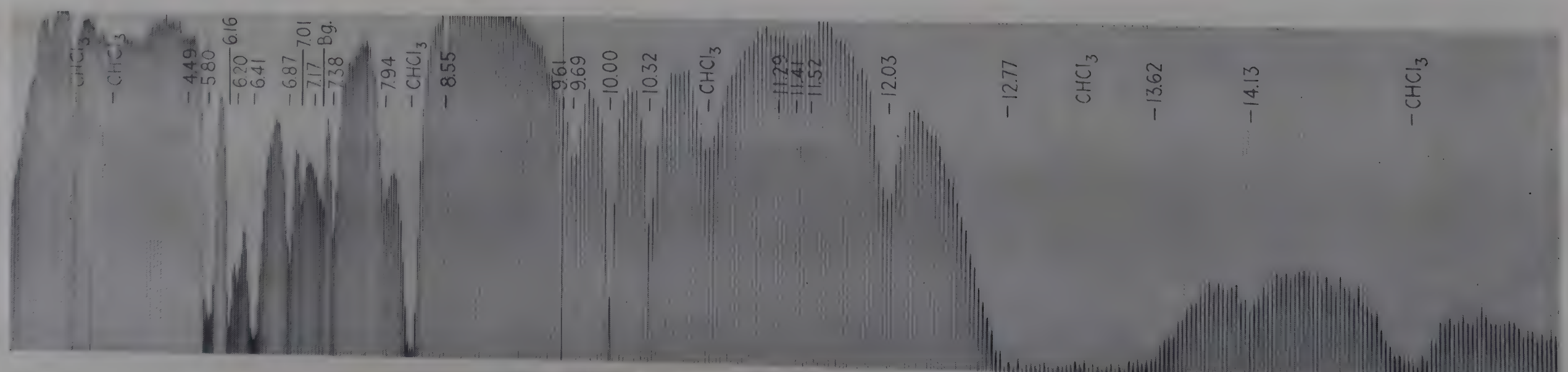


PLATE 346a. Preparations: Chloroform solution 0.02 mm

TRIETHYLAMINE OXIDE

$(C_2H_5)_3N{=}O$

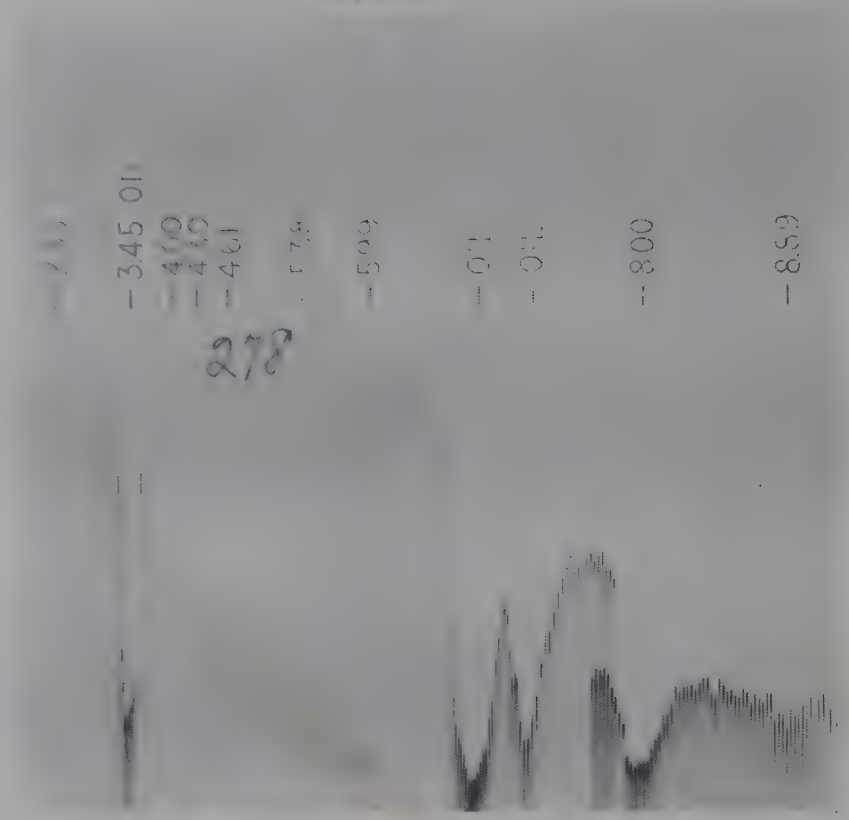


PLATE 347. Preparations: Oil paste

CARBON TETRACHLORIDE

CCl_4

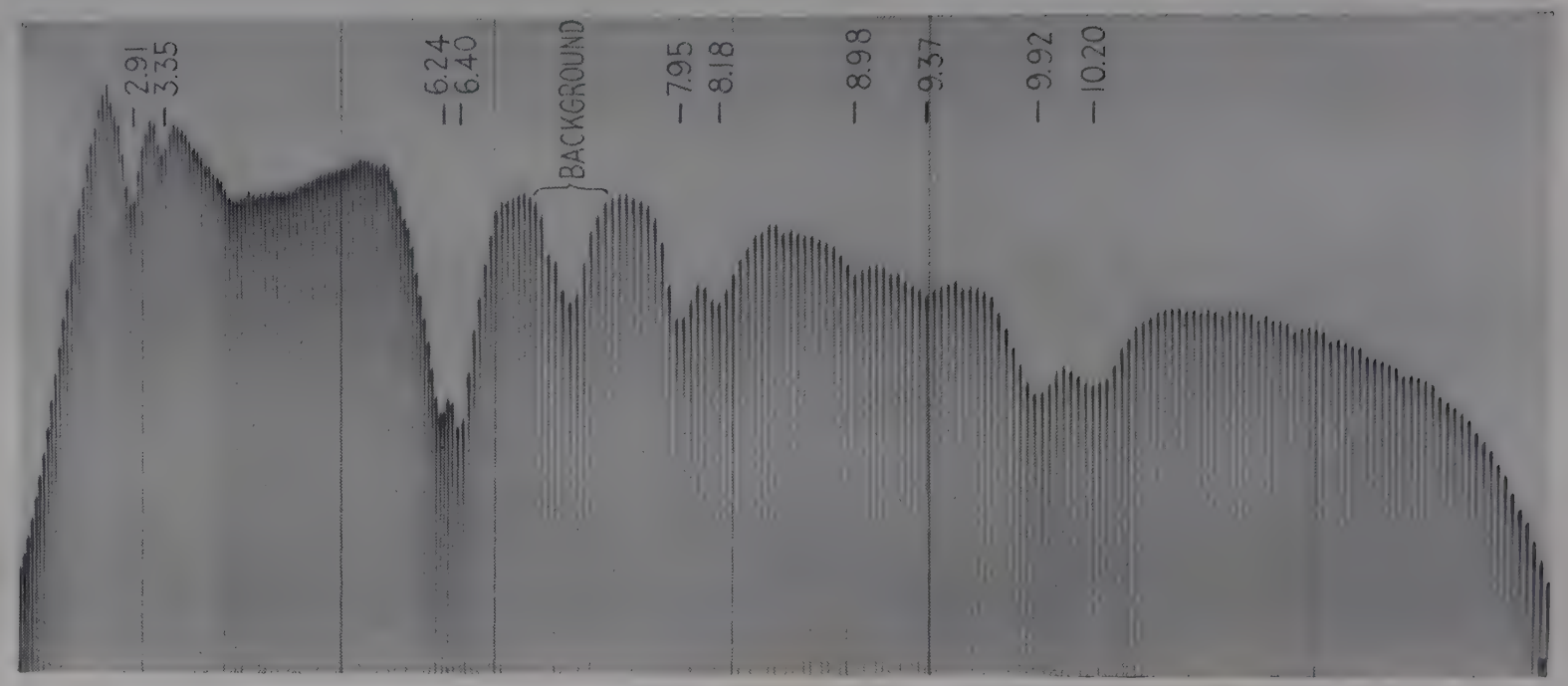


PLATE 355. Preparations: 0.10 mm.

n-HEXADECANE

$CH_3-(CH_2)_{14}-CH_3$

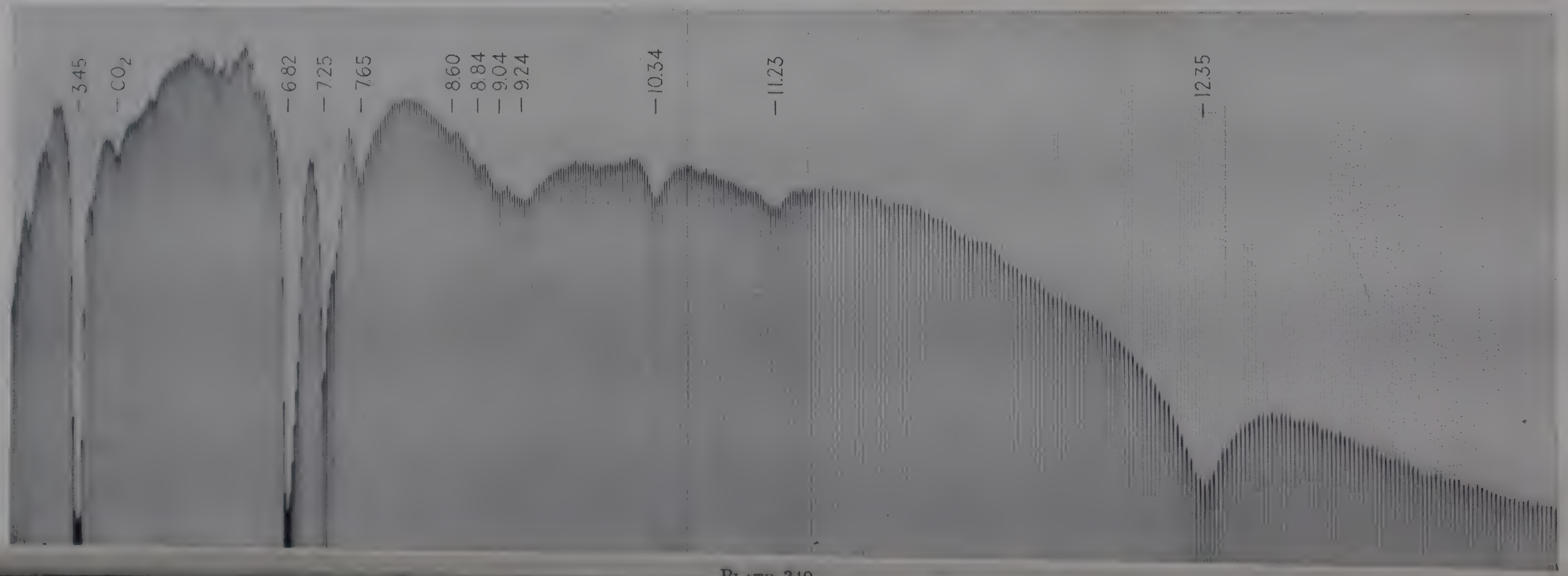


PLATE 349

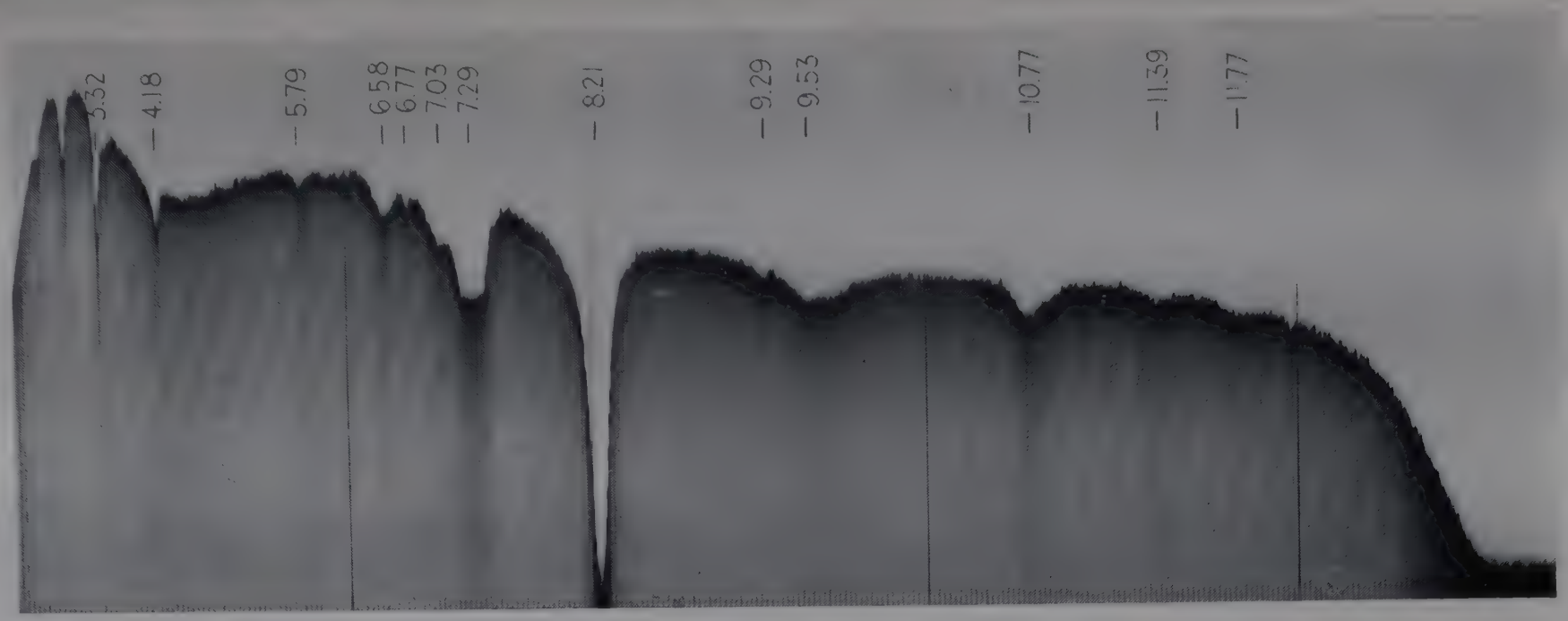


PLATE 352. Preparations: 0.015 mm.

CHLOROFORM

$CHCl_3$

(Both Plates)

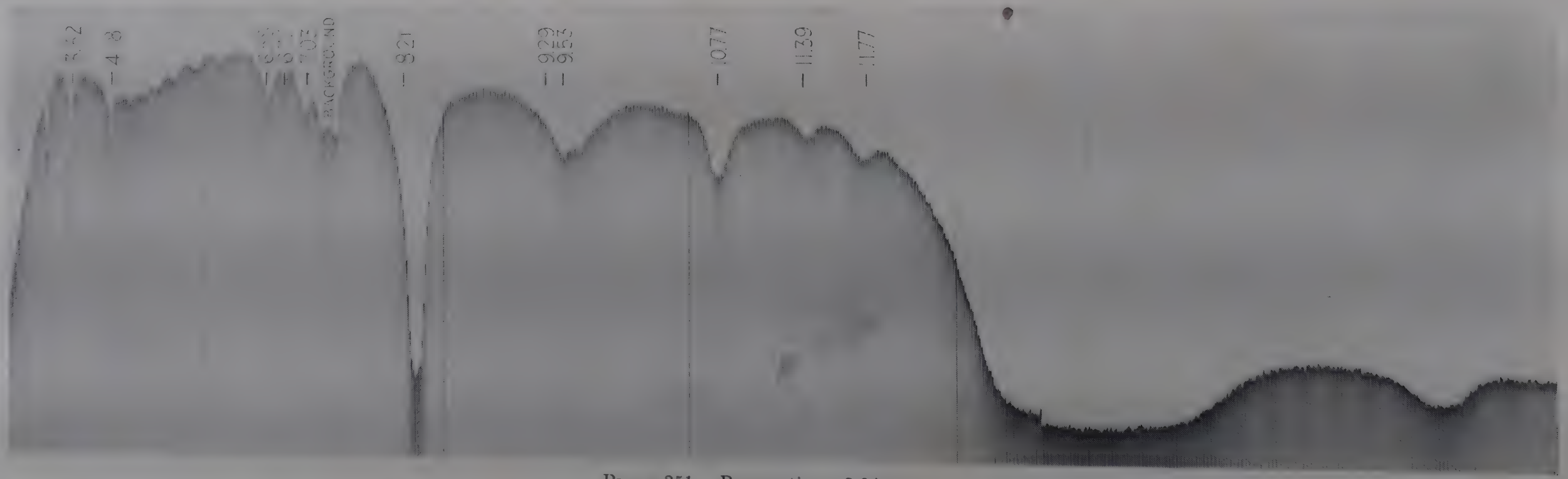


PLATE 351. Preparations: 0.04 mm.

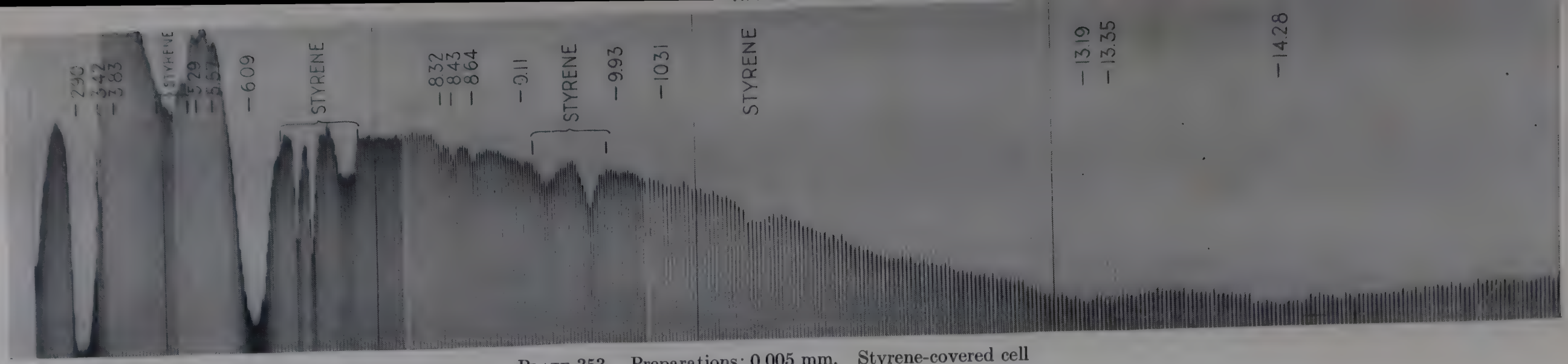


PLATE 353. Preparations: 0.005 mm. Styrene-covered cell

WATER, HEAVY (D_2O) 99.5%

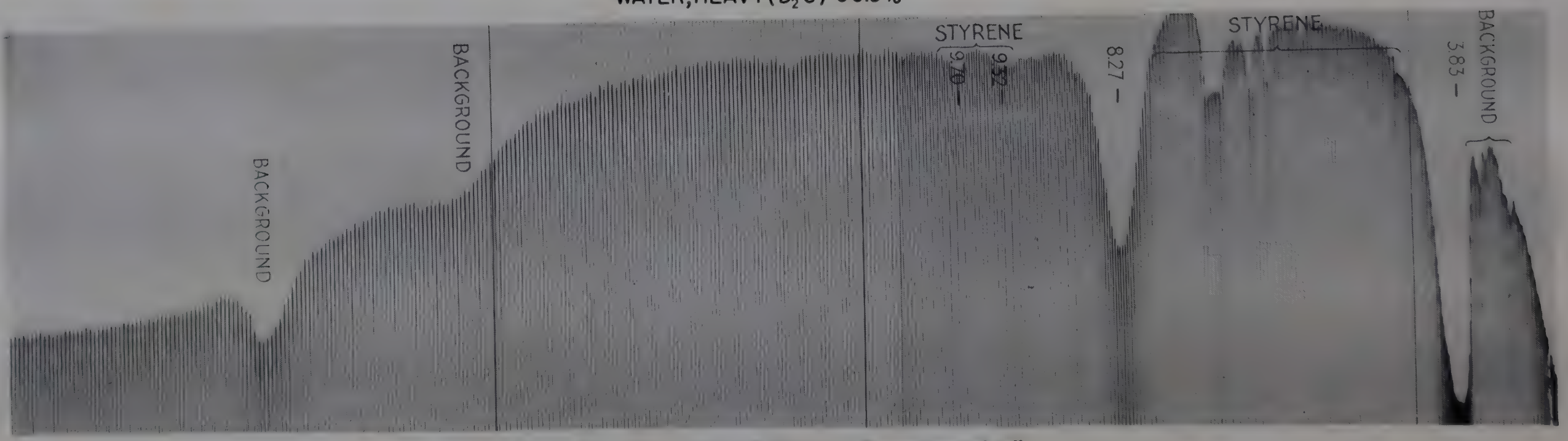


PLATE 354. Preparations: 0.005 mm. Styrene-coated cell

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